Chem Ed

EDITORIALLY SPEAKING

The need for college and university chemistry teachers is getting greater. All who have tried to staff chemistry faculties have sensed this; definite figures have been accumulated by the National Education Association. (*See* "Teacher Supply and Demand in Universities, Colleges, and Junior Colleges," available from NEA at 1201 16th Street N. W., Washington 6, D. C.; also: *Chemical and Engineering News*, July 13 (1959) p. 100.) The most disturbing fact in the collected data is that 253 openings in present physical science faculties were unfilled during the last two years. The look to the future when increased enrollments will compound the problem adds further concern.

Here is a problem, a challenging problem, which no chemical educator can ignore. It is tossed right into his classroom and laboratory. (We refrain from saying "tossed into his lap," for no chemistry teacher who is on his toes has a lap!) One of the lessons which machines can teach human society is the principle of feedback. This problem is a perfect example. Recognition of a future problem should modify present training. Action today may minimize trouble tomorrow.

Where are the college and university chemistry teachers of the future coming from? The obvious answer is that they are now either chemistry graduate students or undergraduate chemistry majors who are planning to go to graduate school. How many of these future teachers have made their decisions to enter academic life? For this there is no obvious answer, only speculation. We doubt that many are sure before the latter years of graduate school. We venture to guess that if a group of first-rate college and university professors were polled, more would indicate that they chose first to be chemists and then were attracted to teaching than would say that the order of their decisions was the reverse.

No choice of career can be made without experience. Although all agree that experience is a great teacher, we believe that the twist of the aphorism, "Teaching is a great experience," has real bearing on this problem. There are bound to be fewer teaching chemists in the future if present students are not encouraged to try teaching under good conditions. An even more alarming factor is that a larger proportion of present students is being denied the experience of teaching.

The present trend of offering bigger and bigger stipends for less and less obligation from the graduate fellowship holder is undermining the supply of teachers. It is a saddening new experience for college professors to find their good students shopping around for the best deal and choosing a graduate school accordingly. A further evil associated with the overabundance of sponsored data-collecting in place of free-wheeling fundamental research is the seducing of good potential teachers away from duties in quiz and laboratory classes. In later years, too, chemical education will be a mystery to these chemists. It may remain a realm inhabited by drudging "suckers." More than likely, the frustration of never having tried it will make it a greener-grass paradise on the other side of the campus fence.

We feel that the problem is so serious that chemical educators in general and chairmen of graduate faculties in particular should make sure that every fellowship or assistantship available to beginning graduate students require the recipient to do some teaching. In some cases, this period of service as a teacher should be postponed. Generally, however, the latter years of the graduate program should be devoted to uninterrupted research. The important thing is that some teaching belongs in the graduate training of every chemist.

By "teaching" we mean some genuine classroom responsibility, not mere routine paper grading. The enthusiasm of the teacher is for the personal contact which results in the joy of watching a mind develop. Seldom is the developing limited to the mind of the freshman. We are sure that graduate students need the challenge of knowing their subject thoroughly enough to teach it to someone else. There are no more penetrating questions asked anywhere than in the class of active-minded freshmen. Answering such questions as, "Why do *you* believe Avogadro's hypothesis is correct?" makes chemists out of graduate students. Realizing that this is what goes on in the classroom may be just the experience that will make much needed future chemical educators out of graduate chemists.

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The Chemistry of Molecular Shapes

The Nichols Medallist is invited to present some phase of his research program at the Award Dinner. Such an open invitation is very pleasant. However, it does throw upon the speaker the necessity of making a difficult choice between his offspring. Although one may love all of his offspring equally well, it is probable that the first-born occupies an especial niche in one's affection. It is on this basis that I have elected to present at this occasion our studies of the influence of molecular shape upon chemical behavior.

Our studies in this area began some 20 years ago. At that time the place of steric effects in organic theory was a very low one indeed. Thus, the excellent book published in 1940 by Professor Louis Hammett, your Nichols Medallist for 1957, played a dominant role in the development of theoretical organic chemistry in this country (*1*). Yet steric effects are conspicuously absent from its pages. Perhaps the prevalent view of the times is best expressed in the words of a textbook published in 1941: "Steric hindrance. . .has become the last refuge of the puzzled organic chemist" (*2*).

The situation had not always been so unfavorable. Beginning with the initial studies by Kehrmann in 1889 (*3*) and by Meyer in 1894 (*4*), steric effects had occupied a respectable place in organic theory. In 1928 such effects were considered of such importance that Cohen devoted a major fraction of his advanced treatise to this topic (*5*).

The immense success achieved by the electronic theory, as developed by Stieglitz, Robinson, and Ingold in the 1920's and 1930's led naturally to the attempt to account for all chemical behavior in terms of electronic effects (*6*). It was apparent that if steric effects were again to receive serious consideration as a major factor in chemical theory, it would be necessary to obtain quantitative, rather than qualitative, data on steric phenomena. A new tool was needed.

Molecular Addition Compounds—A Powerful Tool

The ionization of simple acids and bases has played a major role in the development of modern theories of organic chemistry. Indeed, many of the currently accepted theoretical concepts receive their most direct and best confirmation from acid-base phenomena (*7–9*). It is probable that the major role which this reaction has played in the development of organic theory is due not to any inherent importance of the ionization reaction, but rather to the lack of other simple reversible reactions of wide applicability.

It was pointed out by G. N. Lewis that the essential process in the ionization of classical acids and bases is the coordination of the proton with the free electron pair of the base (*10*). He suggested, therefore, that molecules such as boron trichloride and stannic chloride, which also possess the ability to accept the electron pair of a base, should also be considered acids. Irrespective of whether this definition is accepted, it is apparent that the coordination of such Lewis acids with bases represents a simple reversible process of far greater versatility than the original reaction involving the transfer of a proton.

$$H^+ + :Base \rightleftharpoons H:Base^+$$
$$^1/_2(BH_3)_2 + :Base \rightleftharpoons H_3B:Base$$
$$BF_3 + :Base \rightleftharpoons F_3B:Base$$
$$BMe_3 + :Base \rightleftharpoons Me_3B:Base$$
$$AlMe_3 + :Base \rightleftharpoons Me_3Al:Base$$
$$GaMe_3 + :Base \rightleftharpoons Me_3Ga:Base$$

In studying molecular addition compounds, we have the possibility of introducing wide variations in the structures of both components. Consequently, we are in a position to study in detail the effect of structure and of substituents upon the stability of the molecular addition compounds. In this way, it is possible to evaluate the importance of the classical electronic effects, induction and resonance, as well as steric effects arising from the conflicting steric requirements of the two components.

There is an important additional advantage in the study of these systems. Classical acid-base reactions must be studied in water or related solvents. Interpretation of the results is frequently rendered difficult because of the difficulty of separating solvation effects from the structural interactions under examination. On the other hand, molecular addition compounds can be examined in the vapor phase or in non-polar solvents, greatly simplifying the analysis of the data.

The proton is a charged particle of negligible steric requirements. As long as organic theory concerned itself primarily with the factors controlling the addition or removal of a proton from an organic moiety, it was natural that the theory should emphasize the role of the electrical factor in organic phenomena to the detriment of the steric factor. Extension of the study of acid-base phenomena to Lewis acids with varying steric requirements has led to a clearer appreciation of the role of the steric factor in organic theory.

Steric Effects in Acid-Base Interactions

The ability to vary independently the steric requirements of either the base or the reference acid makes possible a systematic study of the importance of steric effects in acid-base interactions. For example, pyridine, 2-picoline, and 2,6-lutidine constitute a series of bases of increasing steric requirements. The proton, borane, boron trifluoride, and trimethylboron likewise

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constitute a series of acids of increasing steric requirements. A quantitative examination of the acid-base interactions between these substances should permit a decision as to whether steric effects constitute a significant factor in such reactions.

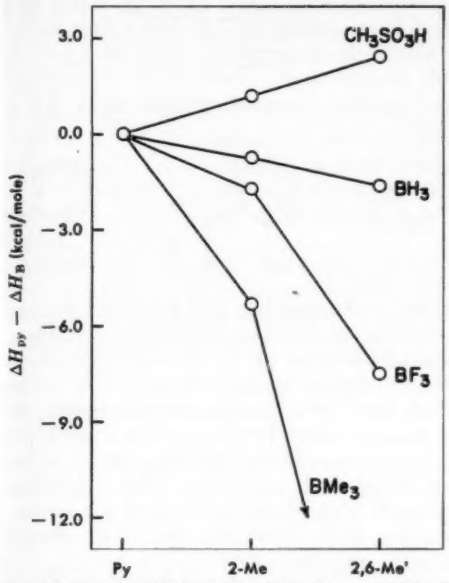


Figure 1. Relative strengths of pyridine, 2-picoline, and 2,6-lutidine with reference acids of increasing steric requirements.

In aqueous solution, pyridine exhibits a pK_a value of 5.17. The introduction of a methyl group in the 2-position raises the pK_a value to 5.97. This increase in base strength is attributed to the inductive effect of the methyl substituent. The second methyl group in 2,6-lutidine raises the pK_a value to 6.75. The fact that the first methyl group increases the pK_a value by 0.80 unit, and that the second has an essentially identical effect (+0.78 unit), indicates that there is no significant steric effect in the transfer of the proton to the heterocyclic nitrogen atom in these three bases. Presumably the steric requirements of the proton are so small that significant steric interactions are absent, even in the 2,6-lutidinum ion (*11*).

In the same way, it is observed that the heat of reaction of these bases with methanesulfonic acid in nitrobenzene solution rises from 17.1 kcal/mole for pyridine to 18.3 for 2-picoline, to 19.5 for 2,6-lutidine. Again the regular increase in ΔH of 1.2 kcal/mole per methyl group argues for the essential absence of steric interactions (*12*).

The situation changes when we examine the reaction of diborane with these bases. Instead of an increase predicted for 2-picoline on the basis of the inductive effect of the 2-methyl substituent, there is observed a *decrease* of 0.7 kcal/mole. Moreover, the two methyl groups in 2,6-lutidine result in a larger decrease of 1.6 kcal/mole. In other words, the change from the minor steric requirements of the proton to the much larger steric requirements of borane has resulted in a reversal from the original order of base strength, pyridine < 2-picoline < 2,6-lutidine, to the opposite order, pyridine > 2-picoline > 2,6-lutidine (*13*).

Consideration of the molecular dimensions of boron trifluoride and trimethylboron leads to the conclusion that the steric requirements of these acids should be much greater than those of borane. Indeed, the heats of reaction of boron trifluoride with 2-picoline and 2,6-lutidine are 2.2 and 8.5 kcal/mole less than the calculated values (*14*). Moreover, the heat of reaction of trimethylboron with 2-picoline is 5.9 kcal/mole less than the estimated value and no reaction is observed with 2,6-lutidine (*15*).

The changing orders of base strengths of these three bases with the increasing steric requirements of the reference acids are represented graphically in Figure 1. It is apparent that the steric interactions increase markedly, both with the increasing steric requirements of the base, Py < 2-MePy < 2,6-Me_2Py, and with the increasing steric requirements of the reference acid, $H^+ < BH_3 < BF_3 < BMe_3$.

It does not appear possible to account for these results in terms of any known electronic effects of the different reference acids. Consequently, it appears safe to conclude that these phenomena must be due to the conflicting steric requirements of the acids and bases and that such steric effects must be important factors in acid-base interactions involving reference acids of significant steric requirements.

Steric Effects Involving the Proton

Conceivably, the steric effects of the base might be increased to such a magnitude that steric effects involving the proton might become significant. Accordingly, we synthesized a number of pyridine bases with bulky alkyl substituents in the 2- and the 6-position. The final member of this group, 2,6-di-*t*-butylpyridine, possesses highly interesting and unusual properties. It reacts with hydrogen chloride, but not with boron trifluoride, thus providing a simple method of distinguishing between protonic and Lewis acids. The base fails to react with methyl iodide. On the other hand, in contrast to less sterically hindered bases, it reacts readily with sulfur trioxide (at −10°C in

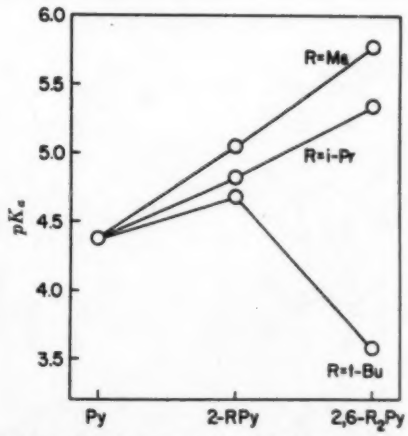


Figure 2. Effect of alkyl groups in the 2,6-positions on the strengths of pyridine bases (in 50% ethanol).

liquid sulfur dioxide) to form a nuclear-substituted sulfonic acid. Apparently, with addition to the nitrogen atom effectively blocked by the two *t*-butyl groups, the electrophilic reagent readily attacks the heterocyclic nucleus (*16*).

The pK_a values of 2,6-diisopropyl- and 2-*t*-butyl-

6-isopropylpyridine are perfectly regular and agree with the values calculated from those of the simpler derivatives. However, 2,6-di-*t*-butylpyridine is 1.4 pK_a units weaker than the calculated value (Fig. 2). This result suggests that the steric requirements of the lone pair on the nitrogen atom must be less than those of the proton with the bonding electron pair.

Methyl groups in the *meta* or *para* positions of aniline bases increase the base strength, a change which is consistent with the postulated inductive effect of alkyl groups. In the *ortho* position, however, such groups considerably decrease the base strength. Moreover, *t*-butyl groups, as in *o*-*t*-butyl- and 2,6-di-*t*-butylaniline, bring about a much sharper decrease in the strength of the substituted bases. These unusual effects of *ortho* substituents have been attributed to the increase in steric requirements of the $—NH_2$ group in its conversion to the $—NH_3^+$ group. Strains resulting from the conflicting steric requirements of $—NH_3^+$ group and the alkyl substituents in *ortho* positions would provide a driving force for the loss of a proton from the anilinium ion (*17*).

The $\gtrless NH^+$ group in the pyridium ion and the $—NH_3^+$ group in the anilinium ion are doubtless strongly associated with a sheath of solvating water molecules. To what extent it is necessary to consider this sheath of water molecules in estimating the steric requirements of the protonated groups is not yet clear (*18*, *19*).

Strained Homomorphs

Study of the stability of molecular addition compounds readily makes available data on the steric strains present in these systems. For example, the fact that the heat of reaction of trimethylboron with 2-picoline is 5.9 kcal/mole less than the corresponding value for 4-picoline is attributed to 5.9 ± 0.2 kcal/mole of steric strain present in this structure. Similarly, the heat of reaction of diborane with 2-*t*-butylpyridine is 6.3 ± 0.2 kcal/mole less than the corresponding value for 4-*t*-butylpyridine. Consequently, it appears that the strains in these related molecules are very similar.

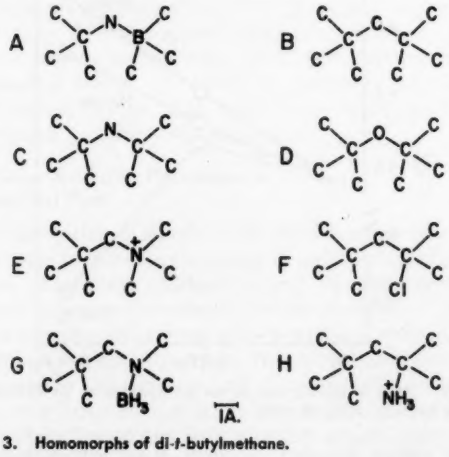
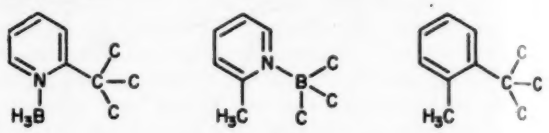


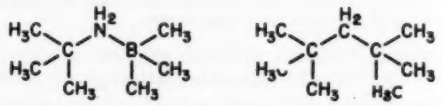
Figure 3. Homomorphs of di-*t*-butylmethane.

Molecular addition compounds are relatively rare substances, which are only infrequently encountered by chemists in their work. It is pertinent to inquire whether the strains present in molecular addition compounds can be simply related to the strains present in other systems of similar structures.

Fortunately, the heats of combustion of the isomeric *t*-butyltoluenes have been measured recently. The results show the *ortho* isomer to be less stable than the *meta* and *para* isomers by 5.6 ± 0.8 kcal/mole (*20*). Thus, within the experimental uncertainty of the individual measurements, these three related systems possess identical strains of approximately 5.9 ± 0.2 kcal/mole.



Similarly, *n*-butylamine and *t*-butylamine are primary amines of similar base strengths. Consequently, it would be predicted that their addition compounds with trimethylboron should exhibit similar stabilities. In actual fact, *t*-butylamine-trimethylboron, with a heat of dissociation of 13.0 kcal/mole, is far less stable than *n*-butylamine-trimethylboron, with a heat of dissociation of 18.4 kcal/mole. The discrepancy of 5.4 kcal/mole is attributed to steric strain arising from the crowding of the two bulky groups attached to the central nitrogen atom (*21*).



The structure of di-*t*-butylmethane is quite similar to that of the addition compound. The covalent radius of nitrogen is slightly smaller than that of carbon, while that of boron is slightly larger. With the boron-to-nitrogen distance almost identical to the carbon-to-carbon distance, it is of interest to compare the strain in the hydrocarbon with that in the addition compound.

As a result of the precise work carried out at the National Bureau of Washington on the combustion of hydrocarbons, it is now possible to calculate the heat of combustion of any simple hydrocarbon with considerable precision. The heat of combustion thus calculated for di-*t*-butylmethane turns out to be 5.2 kcal/mole smaller than the experimental value. It therefore appears that here also the strain in the molecular addition compound agrees with the strain in the corresponding hydrocarbon to within the precision of the measurements.

Consequently, it appears safe to postulate that molecules which are closely related in this way will possess very similar strains. The term "homomorph" has been proposed for molecules which have similar molecular dimensions.

Some typical homomorphs of di-*t*-butylmethane are shown in Figure 3.

It is of special interest to contrast the behavior of neopentyldimethylamine in its reaction with methyl iodide and that of 2-chloro-2,4,4-trimethylpentane in solvolysis. We are accustomed today to large steric effects associated with branching at the reaction center or with branching one atom removed from the reaction center. However, in neopentyldimethylamine the

branching is two atoms removed, and no large difference in steric effects might have been anticipated in the reactions of methyl iodide with *n*-butyldimethylamine and with neopentyldimethylamine. In actual fact, the latter reaction is the slower by a factor of 100. This is explicable only on the basis that the formation of the quaternary salt results in the introduction of the strain postulated to be present in all homomorphs of di-*t*-butylmethane and the molecule therefore resists the transformation (*21*).

The solvolysis of tertiary chlorides proceeds through an ionization into the carbonium ion. Accordingly, this should result in a decrease in the steric strain. On this basis the chloride, 2-chloro-2,4,4-trimethylpentane, should exhibit an enhanced rate of solvolysis, and such is observed.

In other words, whenever the strain present in the reactants is increased in forming the transition state, the reaction is sterically hindered. Whenever the strain present in the reactants is partially or totally

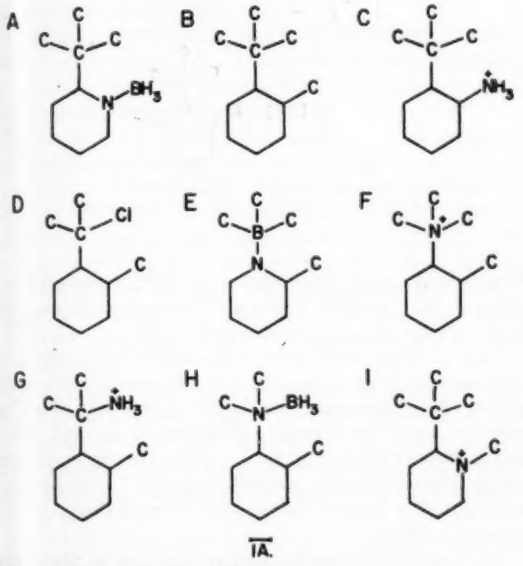


Figure 4. Homomorphs of *o*-*t*-butyltoluene.

relieved in the transition state, the reaction is sterically assisted.

It is of interest to point out that steric effects in the past had been considered to be synonymous with steric hindrance. The proposal that steric effects may assist as well as hinder chemical reactions (*22*) has now been clearly established. Consequently, it should be generally understood that the term steric effects covers both sterically hindered and sterically assisted reactions.

Interesting consequences of the strain are observed in the various homomorphs of *o*-*t*-butyltoluene (Fig. 4). Unfortunately, time will not permit their discussion here.

In the case of 2,6-dimethyl-*t*-butylbenzene (Fig. 5), the strains are so large that no authentic homomorph of this type has yet been reported.

The available results and estimated strains in various homomorphic systems are summarized in Table 1. These early results indicate that there will develop a chemistry of molecular shape of considerable interest and importance.

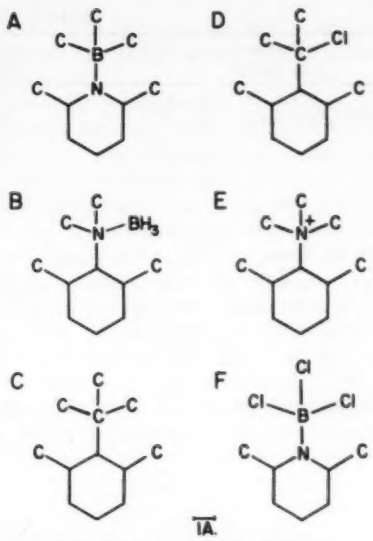


Figure 5. Homomorphs of 2,6-dimethyl-*t*-butylbenzene.

Steric Requirements of Alkyl Substituents

The steric requirements of the substituents, H, Me, Et, *i*-Pr, and *t*-Bu, might have been expected to increase regularly. However, with reference acids of significant steric requirements there is observed a marked increase in steric effect with the introduction of the methyl group in the 2-position, but little further effect as the alkyl group is varied to ethyl and isopropyl. Only with *t*-butyl is a large additional effect observed (Fig. 6).

This apparent large difference in the steric requirements of the four alkyl substituents is attributed to the ability of the ethyl and isopropyl groups to rotate in such a way as to minimize the steric interactions with the reference acid. Consequently, the steric effects of these two groups in these systems is but little larger than that of the methyl substituent. On the other

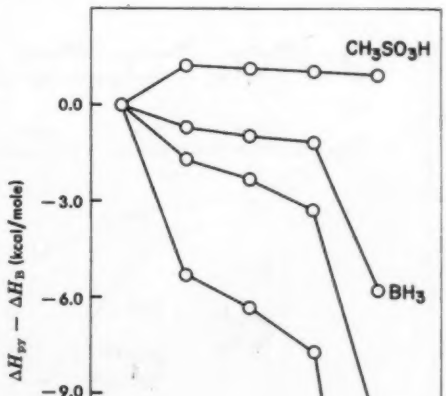
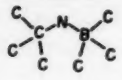
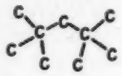
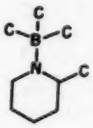
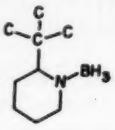
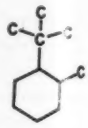
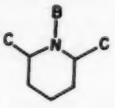
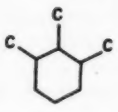
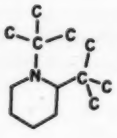
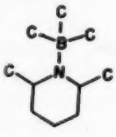


Figure 6. Relative strengths of pyridine and the 2-alkylpyridines with reference acids of increasing steric requirements.

Table I. Steric Strains in Related Homomorphs

Parent homomorph	Assigned strain	Structures (strains in kcal/mole)
Di-*t*-butylmethane	5.3	(5.4)  (5.2) 
o-*t*-Butyltoluene	6.0	(5.9)  (6.3)  (5.6) 
Hemimellitene	2.7	(2.7)  (1.6) 
o-Di-*t*-butylbenzene	25.5	(25.5) 
2,6-Dimethyl-*t*-butylbenzene	24	(24) 

hand, the *t*-butyl group possesses essentially a spherical symmetry and cannot minimize its steric requirements significantly through rotation.

To test this explanation, we synthesized a group of 2,3- and 2,5-dialkylpyridines (Fig. 7). In these molecules the presence of the methyl group in the 3-position should hinder the rotation of the 2-isopropyl substituent and greatly increase its steric requirements. Such an effect is actually observed (*23*).

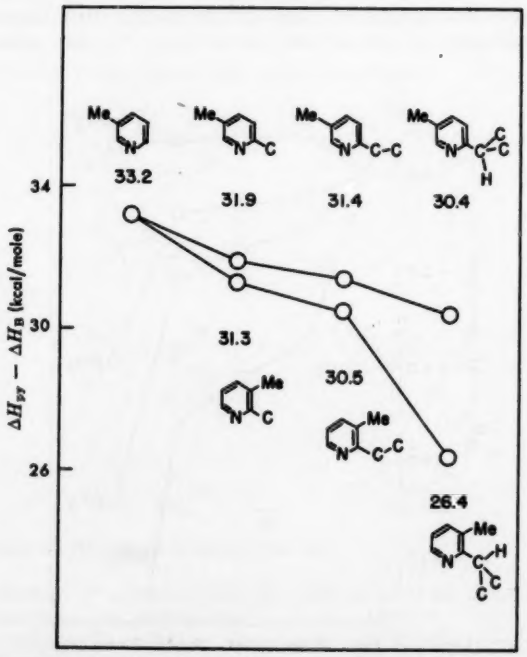


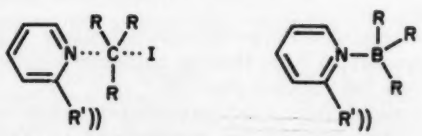
Figure 7. Effect of rotation and hindered rotation on the steric requirements of alkyl groups.

This experimental approach should also permit a quantitative evaluation of the importance of buttressing effects (*24*). Here also we should expect a small difference between the buttressing effects of methyl, ethyl, and isopropyl groups in the 3-position under conditions where free rotation is possible (Fig. 8). However, the presence of a *t*-butyl group should result in a greatly increased effect.

We have been able to confirm the first of these predictions (Fig. 8) (*25*). Unfortunately, the synthesis of 2-methyl-3-*t*-butylpyridine has offered major difficulties which we have only recently overcome (*26*). Consequently, the test of the second prediction is only now under way

Steric Effects in the Transition State

The phenomena observed in typical displacement reactions resemble closely those noted in the behavior of related addition compounds. It was therefore suggested that the steric strains in the transition states of such displacement reactions might be very similar to the strains in addition compounds of related structures.



To test this proposal required considerable data. Accordingly, the following investigations were carried out over a period of several years.

(1) Development of synthetic methods and the synthesis of 2-, 3-, and 4-monoalkylpyridines (R = Me, Et, *i*-Pr, and *t*-Bu) (*27*).

(2) Development of a spectrometric method for measurement of pK_a and its application to the monoalkylpyridines (*11*).

(3) Measurement of the heats of reaction of methanesulfonic acid with the monoalkylpyridines (*12*).

(4) Development of a calorimetric technique and its application to the determination of the heats of reaction of boron trifluoride-tetrahydropyran with the monoalkylpyridines (*14*).

(5) Development of a vacuum-line calorimeter and its application to the determination of the heats of reaction of trimethylboron with the monoalkylpyridines (*15*).

(6) Measurement of the heats of reaction of diborane with the monoalkylpyridines (*13*).

(7) Development of a precise kinetic technique and its application to the reactions of alkyl iodides with the monoalkylpyridines (*28*).

The data, the results of seven Ph.D. theses, are summarized in Table 2. It does not adequately represent the blood, sweat, and tears involved in a closely integrated research program of this kind.

To observe the effect of decreasing steric requirements of the reference acid on the achievement of a linear energy relationship, the values for the heats of reaction of the various reference acids with the pyridine bases are plotted against their pK_a values (Fig. 9). In the case of trimethylboron, pyridine and the 3- and 4-alkyl derivatives define a straight line, but the 2-alkyl derivatives deviate from the line. Moreover, the extent of the deviation varies with the steric requirements of the substituent.

Use of a reference acid of smaller steric requirements, boron trifluoride, moves the points toward the line, and the deviation decreases further with borane as the reference acid. Finally, an excellent linear relationship is achieved with methanesulfonic acid as the reference acid.

If we attempt a similar plot of the log k_2 values for the reaction with methyl iodide against the pK_a values, the results are very similar (Fig. 10). This suggests that the steric effects in the transition state must be related to the steric effects in the related molecular addition compounds.

This conclusion is confirmed by Figure 11. Here also the 2-alkyl derivatives deviate from the line with trimethylboron. The deviations diminish with boron trifluoride as the reference acid. A good linear relationship is achieved with borane as the reference acid. Finally, the use of methanesulfonic acid results in deviations in the opposite direction.

Consequently, there appears to be no significant difference between the rate and equilibrium data. When the steric requirements of the reaction on the vertical axis are greater than those on the horizontal axis, deviations from a linear relationship are observed, and the magnitude of the deviations increases with increasing steric requirements of the reference acid.

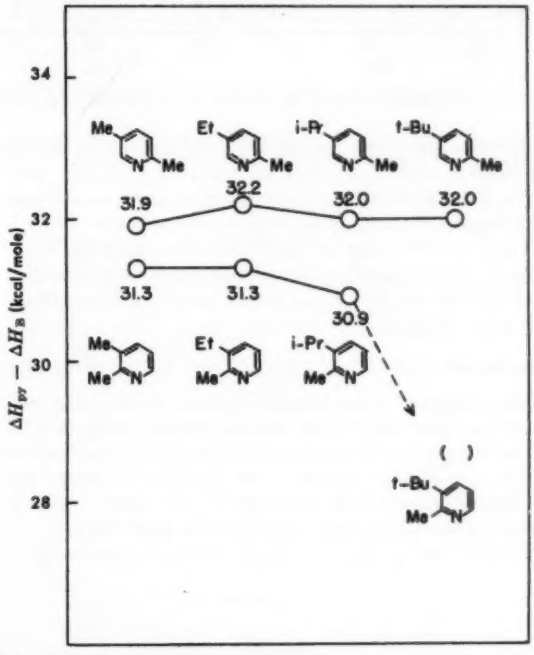


Figure 8. Buttressing effects.

Table 2. Summary of Rate and Equilibrium Data for Reactions Involving the Pyridine Bases

Substituent in pyridine base	pK_a, 25°	Heat of Reaction, $-\Delta H$, kcal/mole				$10^3 k_2$, (25°C) l-mole^{-1}-sec^{-1}	E_{act}
		CH_3SO_3H[a,b]	$1/2(BH_3)_2$[a,c]	BF_3[a,d]	BMe_3[a,e]		
Hydrogen	5.17	17.1	17.9	32.9	21.4	34.3	13.9
4-Methyl	6.02	18.4	18.5	33.4	22.0	76.0	13.6
4-Ethyl	6.02	18.3	...	33.2	...	77.7	...
4-Isopropyl	6.02	18.4	...	33.3	...	76.7	...
4-*t*-Butyl	5.99	18.3	...	33.2	...	75.7	13.7
3-Methyl	5.68	17.8	18.2	33.2	21.7	71.2	13.6
3-Ethyl	5.70	18.1	...	33.1	...	76.1	...
3-Isopropyl	5.72	18.0	...	33.2	...	81.0	...
3-*t*-Butyl	5.82	18.2	...	33.5	...	95.0	...
2-Methyl	5.97	18.3	17.2	31.2	16.1	16.2	14.0
2-Ethyl	5.92	18.2	16.9	30.6	15.1	7.64	14.2
2-Isopropyl	5.83	18.1	16.7	29.6	13.7	2.45	14.8
2-*t*-Butyl	5.76	18.0	12.1	22.7	0	0.0080	17.5
2,6-Dimethyl	6.75	19.5	16.3	25.4	0	1.45	15.1
2,4,6-Trimethyl	7.59	20.7	...	26.4	...	3.75	14.8

[a] Nitrobenzene solution.
[b] Reaction: CH_3SO_3H (soln.) + Py (soln.) = $PyH^+{}^-O_3SCH_3$ (soln.).
[c] Reaction: $1/2B_2H_6$ (g) + Py (soln.) = Py: BH_3 (soln.).
[d] Reaction: BF_3 (g) + Py (soln.) = Py:BF_3 (soln.).
[e] Reaction: BMe_3 (g) + Py (soln.) = Py:BMe_3 (soln.).

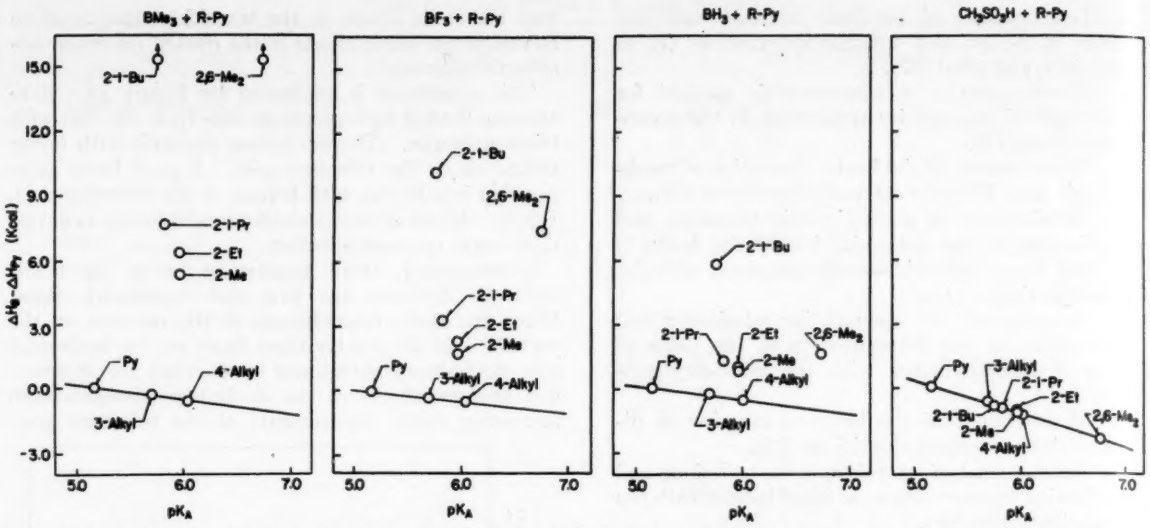


Figure 9. Relationship between the strengths of the pyridine bases and their heats of reaction with reference acids of varying steric requirements.

Only when the steric requirements of the two reactions are similar (ΔH, CH_3SO_3H versus pK_a, and ΔH, BH_3 versus $E_{act}CH_3I$) do the data define satisfactory linear relationships including the 2-alkyl substituents.

These results suggest that molecular addition compounds of the pyridine bases may serve as reasonably good models for transition states involving these bases and alkyl halides.

Conclusion

The study of molecular addition compounds has provided a potent tool for the investigation of steric effects. We no longer need to discuss steric effects in qualitative terms. In many systems it is possible to assess the steric interactions with considerable confidence. Steric effects are no longer the stepchild of organic theory.

This altered position of steric effects is the result of the investigations of numerous workers. In conforming to the request of the New York Section, I have reviewed our own contributions to the present recognition of the role of steric effects in chemical behavior. In so doing, it was not possible to pay tribute to the numerous other workers who have made major contributions to the field and who have completely altered the opinion prevailing in 1940 with regard to the importance of steric effects as a factor in chemical behavior (*29*). In conclusion, I wish to take this opportunity to express my great debt to my capable and enthusiastic co-workers who are primarily responsible for the studies presented here.

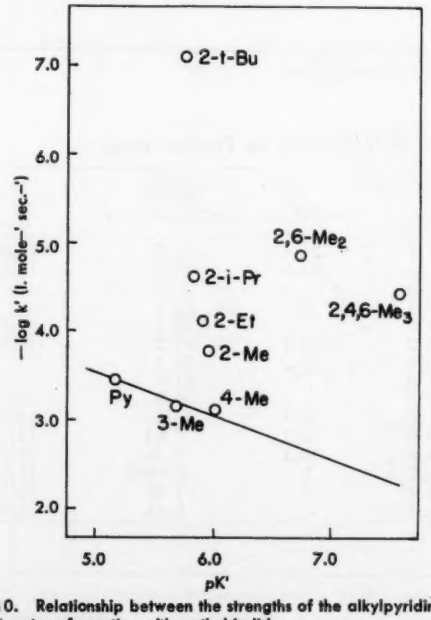


Figure 10. Relationship between the strengths of the alkylpyridine bases and their rates of reaction with methyl iodide.

Acknowledgment

The studies reported in this paper were in large part supported by grants from the National Science Foundation (G975, 2752, 6273). This assistance is gratefully acknowledged.

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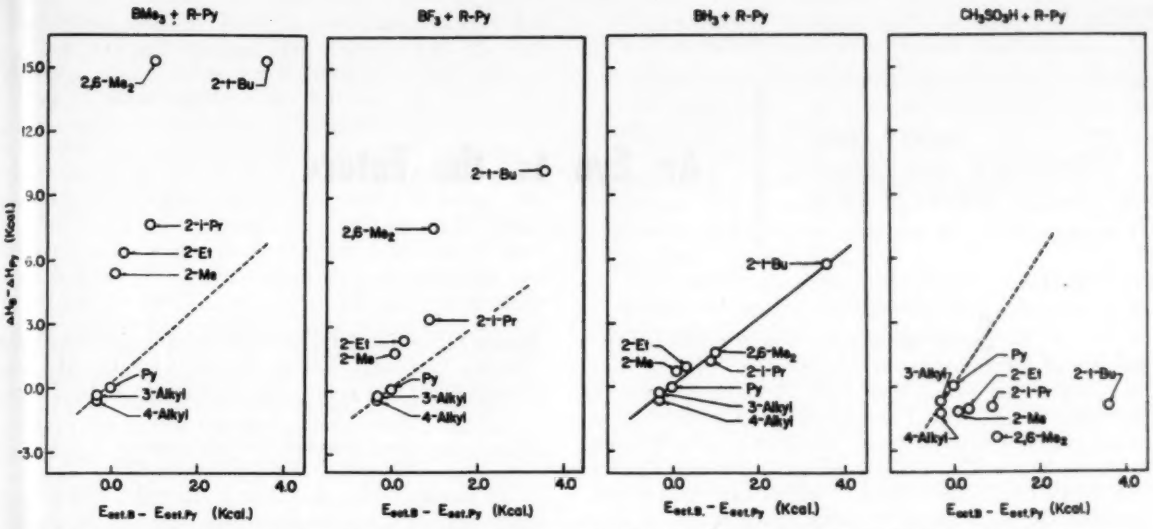

Figure 11. Relationship between the strengths of the pyridine bases and the energies of activation for their reaction with methyl iodide.

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Safety in Amateur Chemistry

With so many adolescents injuring themselves in attempts to make and fire rockets these days, it is heartening to know that there is an organization specifically interested in guiding amateur experimenters along worthwhile endeavors which are safe.

The Amateur Chemist, whose mailing address is Westwood, Lassen County, California, is an altruistic organization devoted to the stimulation of the hobby of amateur chemistry in adults as well as adolescents, with a strong emphasis on safety. There are neither dues nor subscription fees; the monthly paper is entirely free.

This organization was founded almost ten years ago by Dr. Craig Burns who began building his own amateur chemical laboratory at age 12 and later graduated in chemistry from the University of Minnesota. From there he continued his studies to graduate in medicine from the same University in 1944, and has subsequently received an additional degree from the University of California in Industrial Health. At present he is a consultant for the California State Department of Public Health in Occupational Health and Diseases. It is only natural that Dr. Burns, as editor of *The Amateur Chemist*, should be concerned with health and safety problems of amateur chemists, see this Journal, **33**, 508 (1956).

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Appleton, Wisconsin

An Eye to the Future

Some months ago I was asked for the subject of my remarks on this occasion. Up to that moment I had given very little thought to what I intended to say. But I was quite sure I would not be much concerned with water which had already gone over the dam and so I remarked quite casually, "let us call it 'An Eye to the Future,' " which I thought would provide me with ample working space to go in any direction as long as it was ahead. In preparing the talk, however, I found it necessary to add at least as a parenthetical phrase in my own mind—"with an Ear to the Past," for I found it hard to talk about the future without thinking about the past.

Before I get to the subject, let me first pay tribute to the officers and committee members of the Division of Chemical Education. I have worked with several professional organizations and have been closely connected with their committees and programs. I have never worked with a group having a greater sense of dedication and a feeling of concern for a cause than has been shown by those working on the programs of the Division of Chemical Education. Time will not permit much expansion of this statement but it is more than a coincidence that led the National Science Foundation to turn to this group for working leadership for its programs on science education. Names coming quickly to mind in this connection include those of W. E. Morrell, active in the early institute program of the Division and now its alternate councilor; G. W. Smith, for three years secretary and its current chairman; E. L. Haenisch, former Division chairman who sparked our Visiting Scientists Program and has been active in many of the conferences held under the supervision of the Division in the early years; W. B. Cook, now chairman of the Institutes and Conferences Committee; J. A. Campbell, another former chairman and active in several committees; Arthur Roe, principally concerned with the Examinations Committee; and L. N. Pino of the Institutes and Conferences Committee. When the ACS was asked by the Fund for the Advancement of Education and Encyclopaedia Britannica Films to participate in a project involving the production of the world's first chemistry course on film they selected our secretary, J. F. Baxter, as the teacher. When the AAAS wanted to study the preparation of high school science and mathematics teachers, they picked another past chairman and present councilor, A. B. Garrett, to head up the work. Our treasurer, E. C. Weaver, started in his term of service in Washington as the MCA's Senior Education Adviser while on sabbatical leave from Phillips Academy. I could run on at length but I hope I have made my point. To paraphrase Robert Frost:

> Their object in living is to unite
> Their avocation and their vocation
> As their two eyes make one in sight.

To continue with this train of thought, I think possibly my own extra-educational activity of greatest interest has been the YMCA. My father was a YMCA Secretary; I have a son who is a YMCA Secretary. My use of the terms "dedication" and "concern" come from this lineage. Over the years I have gone to many conferences of professional workers in the YMCA and have heard them speak about their "concerns" as a prelude to working out a new program set up in response to the "concern." "Concerns" come first, actions follow. Tonight I am going to speak to some of my "concerns" for chemical education.

Lest you think I am going to be a Jeremiah bewailing the sad state of chemical education in this country, let me quickly reassure you. I started out in this field in 1916. I have seen the American chemical industry grow from almost nothing to the number one position in the world. I took a very small part in our feeble beginnings. I watched the rush for the dyes and medicinals brought into the country by the German submarine *Deutchland* in its one trip in 1915 before the United States got into the war and had a feeling of shame for our weaknesses. Because of this, I glory in the achievements of the products of our chemical and engineering education. But nothing is perfect and we had better be realists and do what we can to shore up the weak spots.

My first "concern" has to do with the Division of Chemical Education itself. I have spoken of the dedication of the officers and committee workers. A wonderful spirit of friendship exists among the group. They work together as a team—and it is a big team. The new directory lists about 100 names of workers in this group, or almost 5% of the membership. Our present strength in working together may become our Achilles heel for we need the sparking of new people and new ideas to keep us ever facing forward. A rut serves only to lead where others already have been. It has been called "a coffin with both ends off." We should be blazing new trails. So to the Division I say, let us be plowing new recruits into our activities all the time. If we have more wanting to serve than we can use on our present programs, let us set up new programs in different directions. There is room enough for everyone to get in the act. Let every man make his own place.

The High School Science Teacher

My next "concern" has to do with the science teacher

The 1959 Scientific Apparatus Makers' Award in Chemical Education address given before the dinner meeting of the Division of Chemical Education at the 135th Meeting of the American Chemical Society, Boston, April 6, 1959.

in our high schools. There has been a great deal said in the last ten years about the shortcomings of these teachers. Some of these are attributed to their training, others to other inadequacies for the job. My own experience with high school teachers at summer institutes of one kind or another and in visiting them in high schools, is that many are a lot better under the conditions than they are given credit for being. We tend to forget that a good course in high school chemistry does not come about solely as a result of the work of the teacher. There must be disciplined students, and here I use the term in its broadest sense; there must be an understanding principal and superintendent of schools; it helps to have an informed school board; but of necessity, the scientifically trained people in the community must take a leading part in interpreting the needs of the science teacher to the school boards and to the community in general. Often a good course develops in spite of "feet dragging" by the other contributing groups. But the outstanding course (and who would want less) is generally the result of group understanding.

Since much of the trouble with high school science teaching is laid to inadequate preparation in subject matter areas, let me recall to your mind what is being done currently to stimulate subject matter growth in the high school science teachers. Most important is the series of programs currently being sponsored by the NSF. During the summer of 1958, about 5000 teachers of high school science and mathematics attended 118 summer institutes designed to deepen and broaden their knowledge of their fields. In the summer of 1959 more than three times the number, or close to 17,000 teachers, attended some 320 institutes. Since the total number of science teachers, I think, approximates 155,000, opportunity is being provided in this current year for the improvement in subject matter of a significant fraction of the science teachers in the nation. Other high school teachers are taking advantage of the year-long institutes sponsored by the NSF and have been able to get Master's degrees involving significant amounts of science training. Thirty-two academic year institutes will operate in 1959–60. Another 750 teachers will be awarded summer fellowships for study for advanced degrees; these may run for three summers. Then there are several thousand teachers in 85 in-service institutes. In still another part of the NSF, some 700 teachers will participate in a summer program of "research participation for teacher training" by working in college and university research laboratories. In past summers, industry has operated a similar program with high school teachers taken on as summer workers in industry research and process development laboratories. Local sections of the ACS have been active in developing this program.

Speaking parenthetically, I must confess I am somewhat concerned about the summer program for high school teachers in industry and as the source of my concern I quote from the *Chemical Bulletin* of the Chicago Section of the ACS for February, 1959, page 17.

> Last year the Section office received a total of 161 applications for summer employment, of which 39 were from teachers and 122 from students. These applications were referred to 22 companies, which in December, 1957, had indicated willingness to cooperate with the Section in offering employment to the applicants during the summer. At that time, 7 of the 22 companies expressed interest in employing teachers while 15 indicated they would each hire 1 or more students. Of the 161 applicants, however, *not a teacher was placed*, and employment was found *for only 2 students*.

I wonder whether something like this was nationwide in its spread and if so, whether it has anything to do with the falling off in September, 1958, of freshmen in chemical engineering. Surely we are not going to weaken in our determination to strengthen our scientific resources every time the curve of business activity shows a slight decline preparatory to starting on its next rise.

Also, in past summers, industry has provided money for institutes and conferences for high school teachers. Many of these have been of the two-week variety. How many have been held we do not know, nor how many teachers have been registered. The number must be significant. Any attempt to name companies or colleges would omit some, so it is best not to be too specific. It is my belief from active participation in such programs that more teachers have been helped than we have any idea. In fact, I have been told by some of these that the inspiration of intimate association with fine teachers in two-week conferences has had an influence for better teaching out of all proportion to the time involved. I should like to see the appropriate Division committee again give serious consideration to the promotion of more short conferences of the type so successully sponsored by the Division between 1950–56; these were sponsored in part by industry and in part by the institution. In support of this proposal, I would like to see adequate financial support provided by the NSF. I must confess I would also like to see industry get back into the same act. Those of us who were privileged to be at either Fisk or Kenyon will never forget the stimulation we received from the evening exchanges of experiences as high school and college teachers sat together out on the campus during the warm summer evenings. These short conferences act as catalysts; teachers who feel their weaknesses are encouraged to do something about them.

Finally, *many* high school teachers more or less on their own have gone to summer schools to repair the damage of poor preparation. Too many in this category have ended up by taking courses in methods which do not meet the issue. Now programs are available in many universities just to meet their needs as is shown by the fact that 78 colleges and universities were providing opportunities for high school teachers to gain subject matter Master's degrees in chemistry (and other sciences) in a survey made by a subcommittee of the Committee on Institutes and Conferences just last year.[1]

In view of all of those activities, why should there be a "concern" for the high school science teacher? Let me answer by reading an editorial which appeared last year in the NEACT Newsletter from the pen of a good high school chemistry teacher. This is entitled *Must It Be So?*

> For many of us chemistry teachers another summer of institutes, fellowships, and personally financed summer sessions is about to begin.
>
> We will hob-nob with master teachers, be awed by great scientists, marvel at the finesse of super-demonstrators. We will read deeply, try our hands at experiments we dared not try before, negotiate proofs of invisible molecular conditions with great

[1] *See* J. CHEM. EDUC., **35**, 417 (1958).

personal satisfaction, record pages of notes for future perusal and use. We will be challenged and will meet that challenge. We will be sparked, and will go home inspired. We will have a truly professional summer, and will deeply appreciate the experience.

Then we return to our schools.

For far too many of us the duality of it all then appears.

We cannot find time to perfect those rather complicated, but marvelous demonstrations, for our lab is a homeroom and an activity room and we are in charge of both. We are moved to back-off from these beautiful, theoretical considerations and proofs, for too many who cannot comprehend have found their way into our class. We struggle to work the newly-acquired knowledge into our course, for with the full schedule and pupil load there is very little time for patient, thoughtful organization. We cringe inside, realizing the ineffectiveness of it, as we tell of an excellent experiment to show a chemical phenomenon, for there are too little funds available to purchase necessary equipment. We neglect the gifted for the masses are upon us. We become split personalities, as, at the same time, we try to show those who must be shown and not to show those who should show themselves. Now *we* are dual, for we do all.

MUST IT BE SO???

So here is my specific "concern." Will all the efforts of the high school teachers, the dedicated services of college and university professors serving as instructors and lecturers at these institutes and conferences, the many millions poured into the sparking by industry and by government be in vain by virtue of conditions in the local schools which make any use of the new material impossible due to a lack of time for study and arrangement of experiments and due to a lack of space and equipment? The writer of the above editorial says nothing about salary but stresses only time and equipment. How can we alert the folks back home so that the stimulated science teachers may find the time and facilities and the able students to put into action what they have learned during the summer institute or other program? It need not be so!

I should like to recommend consideration of some of the following approaches:

(1) The preparation of a booklet by the NSF or by the Science Teaching Improvement Program of the AASS or by the NSTA directed toward the amelioration of some of the conditions implied in this editorial. This might be sent to school superintendents and school boards of the participants of summer institutes and conferences at the beginning of the following school year.

(2) The preparation of similar material by the same agencies for the home town papers of the participants as a follow-up of the institute experience.

(3) The setting up of a program of papers and speeches directed toward the pages of the journals of such professional societies as the American Association of School Administrators, Associations of Chief State School Officers, the National Association of School Boards, or the sessions of their meetings.

(4) An editorial in *Chemical & Engineering News* calling attention of ACS members to the problems faced by the high school teachers who are returning from institutes and asking for their help in their own communities.

It is possible that what we need is a program of conferences for school administrators as well as for school teachers, and the Division Committee on Institutes and Conferences might well give consideration to a short conference for school superintendents to talk about their general problems in relation to the teaching of science in the schools. This is not a new idea. In the summer of 1957, the International Paper Company sponsored workshops for teachers of science and mathematics in their mill communities and followed these with workshops for the school superintendents of the communities for which the teachers came. This, it seems to me, is worthy of study.

I have a second "concern" in the area of high school science teaching. This has to do with the high school textbook and teaching aids. Physicists, biologists, and mathematicians are making tremendous efforts to see that their disciplines utilize in the appropriate high school courses the latest and best information and sequence of material. In the case of physics, almost two million dollars have already been spent in this effort. But in chemistry, the only real evidence of any activity along these lines up to last December has been that shown by the committees of the Division which have been responsible for studies made at Reed and Wesleyan in the summers of 1957 and 1958[2] and which in the summer of 1959 sponsored a working conference at Reed to prepare 50 copies of a textbook together with teaching aids and laboratory experiments directed toward *one* new approach to the teaching of chemistry in high schools. There should be other studies made and all of these should be considered to determine how they might be integrated with physics and mathematics developments. If I had time I would read you some of the letters I have been getting this year from high school teachers. At the Wesleyan Conference last summer I casually offered to prepare a newsletter and send it to the members of the conference about every other month. I thought that since only 25 or 30 were at the conference it would require not too much effort. But to my amazement we now have been forced to add another 50 names of high school teachers all over the country who read the JOURNAL OF CHEMICAL EDUCATION and through its pages have heard about the Wesleyan Conference and want to know more about it. While many of these teachers have directed their questions directly to the chemical bond approach, requests have also been made for a twelfth-grade course as a follow-up of the PSSC physics course. This incidentally was one of the recommendations of the Wesleyan Conference. It is my understanding that some conferences have been directed toward other than the chemical bond approach. I would hope that in some way serious consideration be given to what should be covered in the high school and what should be covered in the first year course in college chemistry so that the second is not just an uninspired and uninspiring duplication of the first.

I think we owe it to the forward looking high school teachers to furnish up-to-date textual material as a part of a two-year sequence in which the first year college course furnishes the second year of the sequence. A few of the better secondary schools might be encouraged to give both years, and their students might then be eligible directly for second year college chemistry. Competent members of our college and university chemistry teaching staffs should either review the available texts and speak out boldly in criticism of those which are out of step with the times or they should start fresh if text books are not meeting the needs. Let the best men step forward and offer to work together to produce satisfactory material. This program is one of sufficient importance so that the ACS itself should get behind it with aid from the National Science Foundation.[3] I am

[2] *See* J. CHEM. EDUC., **35**, 54 (1958), and **36**, 90 (1959).

[3] By the time this was presented, a move of this kind had already been initiated; needless to say those in the Division who have shared this concern are delighted.

tired of hearing college and university teachers of general chemistry say they wish "students would come to them without any high school chemistry for they would do better in their courses if they had not already had the high school course"—and then do nothing at all about either the high school course or the one they are teaching. I am sure many of these teachers go over the same material in the same order and with the same experiments as the student has already had in high school. What challenge is there in that for a budding scientist?

Science in the Liberal Arts Colleges

My next "concern" is for the liberal arts colleges, whether they be privately operated schools laying claim in their catologues to being followers of the liberal arts tradition or whether they be state teachers colleges converted by fiat to colleges of arts and sciences and granting liberal arts and sciences degrees.

I have recently made a somewhat extensive investigation of the liberal arts colleges as baccalaureate sources of Ph.D.'s in chemistry for it is and has been one of the proud boasts of liberal arts college speakers generally that they have given undergraduate preparation to science Ph.D.'s out of all proportion to the number of students. This is no longer true, if it ever was. True it is for possibly 75 to 85 of the 625 or so private colleges studied, but in contrast, better than one third of the 625 failed to provide training for even a single Ph.D. in 21 years, and one half the total number trained two or less. For practical purposes this half may be classified as "unproductive." In between the "productive" schools and the "unproductive" schools are the borderline schools of which there are about 240. My concern is first for these borderline colleges and their teachers; what can be done to bring these up to the productive classification? Then next how can we stimulate the unproductive colleges to move up a few steps on the ladder at least to the borderline category? To do this is not simple for it involves other factors than the teacher. The Wooster Conference held in June, 1959, under the sponsorship of the Committee on Institutes and Conferences of the Division should help to determine what our Division might be doing, through its programs, in its committee activities, and the JOURNAL OF CHEMICAL EDUCATION. It may have recommendations to make to other groups in the ACS and to the colleges themselves. In a time like this when we talk about the coming deluge of students, how much better it would be to help to improve those we have before we start a lot of new ones. Let us remember that college teachers can be as much frustrated by their limitations as are high school teachers.

Somewhat the same applies to an even greater degree to certain of the ex-teachers colleges now operating with about the same staffs and administration as they had when they were teachers colleges, even though they are now classified as liberal arts colleges and are authorized to give B.A. and B.S. degrees with full majors in the science fields. As teachers colleges, these institutions had a well-defined objective which was to train elementary and high school teachers. People may quarrel with their methods but not with their quantitative achievements. In a survey just completed in the area covered by the Northeast Wisconsin Section of the ACS it was found that 39 of the 73 teachers of high school chemistry were the product of teachers colleges. As liberal arts colleges, will these schools continue to provide the college training for the elementary and high school teachers of our state? If not, who will? As liberal arts colleges, how will their philosophies and processes change to meet their new status? I think you can sense that I have two concerns for these ex-teachers colleges. The first is whether they will continue to train elementary and high school teachers for our schools, and if so, will their status as liberal arts colleges broaden their recognition of the importance of subject matter material? Can and will they follow the recommendations of Dr. Garrett's Committee of the AAAS[4] which for a chemistry teacher calls for a major of 28 hours with an additional 8 hours of physics and biology, 3 hours of earth sciences, and 12 of mathematics, together with one-half of the student's course time spent in the humanities, social sciences, and professional courses followed by a fifth year of professional education containing some additional subject matter. To me it seems that the sooner we are able to put into practice the recommendations of this committee the better. The alternative will be the extension of the NSF institutes program for high school teachers well into the future for each future year's crop of new teachers. This is expensive in terms of money but, what is more expensive, it is being carried out at some cost to the research programs of the hundreds of college and university teachers who are presently giving up the better part of their summers to serve as directors, staff, and special lecturers on the programs presently under way. They will not do this forever without complaint. The second concern is whether if they are going to stress the liberal arts college feature of their program, these will be true liberal arts colleges in the strictest sense of the word. Such institutions by virtue of their public support can provide Arts degrees at costs substantially below the cost of a private liberal arts college. Soon their graduates in large numbers may be knocking at the doors of the science departments of our graduate schools with all the apparent qualifications for admission. Will these have only form or will they have substance? Traditionally and historically only a few of these schools as teachers colleges have participated in the baccalaureate training of chemistry Ph.D.'s. Publication 582 of the National Research Council—Baccalaureate Origins—lists only 4 institutions out of 147 for example which have given undergraduate training to more than 10 Ph.D.'s in chemistry between 1936 and 1956; 121 would be listed as unproductive, the other 22 would be borderline. In general, any programs to improve the teaching in the liberal arts colleges might well apply to the transformed teachers colleges.

I think we can do something to upgrade the borderline private colleges without spending too much money, but it will take more time, energy, and money to move up the unproductive colleges. The summer institutes and new topical conferences for college teachers of chemistry provide a good starting point. The Visiting Scientists should be very helpful. The Research Participation for Teacher Training will provide new horizons for teachers in unproductive colleges. The DuPont college grants, the wonderful work of the Research

[4] *See* J. CHEM. EDUC., 36, 207 (1959).

Corporation in supporting college research, and assistance provided by other groups like the Petroleum Research Foundation, etc. have set up directional markers. If research is indicated as one approach to productivity, I should like to see some group like the MCA line up in annotated form at intervals lists of research projects suitable for such college teachers as need help in starting research programs. Meetings of associations of liberal arts teachers like the Midwestern Association of Chemistry Teachers in Liberal Arts Colleges have provided very definite stimulation for efforts by colleges to help themselves.[5] Perhaps the Division should give encouragement to the formation of more such informal groups whose meetings are of so much interest and value for the college teachers in attendance. While they do not take the place of the Division and the ACS, they do serve as a starting point for professional relationships with these latter groups. Finally I should like to see the NSF or other foundations initiate the DuPont type of grant for college science departments to help them get under way with faculty research and other creative activities.

I also have a real "concern" for the unproductive institutions which are universities in name, in that they are made up of a number of colleges and give graduate degrees. There is not much difference between a single unproductive college and a federation of unproductive colleges under the name of university. A vigorous interest in science as a career seems to be missing in many of these institutions. At least half of all of the universities when measured against the colleges would not show up to good advantage. Why should not these be just as good breeding grounds for the identification and inspiration of potentially creative scientists as are the other 50%? Far be it from me to suggest programs for their improvement other than to say that they have the same problems as do the unproductive colleges, only in larger measure. The Division might well establish a subcommittee of the Committee on Teaching to study teaching problems in the universities and to establish workshops to recommend programs for unproductive universities.

Develop Creativity in Students

In what I have been saying I hope I have made it clear that while my concerns have been for the schools themselves and their teachers, I do have a very real concern for their students. In a civilization which is steadily becoming more intricate, we continue to treat the students as children. Instead of challenging them, we prod them along the same ruts we made a generation ago. We keep them busy in the laboratory making observations an elementary school student could make and ask them to insert appropriate words in blanks on page after page of laboratory notes, thus depriving them of an opportunity for experience in scientific writing. We scarcely ever seek their participation in planning experiments; sometimes this is true even for doctoral candidates. We sometimes even put a penalty on results which go contrary to approved answers. We emphasize conformity at the expense of creativity. I have a firm conviction based on some experimental proof that the productive schools are also the creative schools (using the term "creative" in its broadest sense). A poor teacher is satisfied with the "what of what the book says;" but a good teacher constantly stresses the importance of knowing not just the "what" but also the "how" and the "why." Descriptive facts form the grist of the poor teacher. While there is nothing wrong with such per se, in addition to them the outstanding teacher challenges the student with quantitative and reproducible experimentation, integration, interpretation, hypothesis. In moments of depression, it sometimes seems as though poor teachers and poor schools are not much better than "no teachers and no schools." The Lincolns left alone will educate themselves. The irony of it all is that it is the student, or his father or some foundation or some friend who pays the bills, who thinks he is buying a first class education, and by virtue of his own ignorance and innocence has sometimes had foisted on him a second or third class education. One approach is for us to give more emphasis to the work of the Committee on Professional Training and do everything we can to urge the schools not on the list to meet the requirements of the approved institutions.

I also have a special concern for the graduate student in chemistry who is unfortunate enough to be only the "slave" or a "pair of hands" for a publication-minded professor. A graduate student who is fortunate to have as his thesis advisor a teacher-researcher will be constantly called upon to use his creative imagination and defend his ideas. The "slave" on the other hand is given a specific assignment to do and after an appropriate number of months or years may be fortunate enough to receive the Ph.D. as an indication of the completion of the contract. I think it has been pretty generally agreed that we need the Einsteins and the Paulings much more than we need the trained research assistant. We should do everything we can in the course of the graduate school program to develop those qualities which lead to a high order of independent thinking. How much longer are we going to tolerate practices which work in just the opposite direction? Too many doctors of philosophy are teaching in colleges today who have never enjoyed a genuine research experience; somewhere in graduate school they have been short changed. These are the teachers the NSF programs should work to activate and to inspire. I do not say this in any sense as a criticism of all graduate education. One has only to look at the productive universities to see good programs. I think the Division of Chemical Education needs more programs dealing with the aims and objectives of graduate education and I am not sure but that the NSF might well give consideration to setting up serious programs in this area. Why are some institutions breeding grounds for genuine scientists while others seem to specialize in turning out "pot boilers?"

New programs come from people who are concerned. We can always expect to have the good ones we develop taken over by agencies better able by virtue of manpower and funds to put our experimental studies into full-scale operation. This should be a cause for rejoicing on the part of the Division for it leaves the committees and the membership free to experiment anew. May the Division of Chemical Education continue to be concerned and continue to do something about these "concerns."

[5] *See* J. CHEM. EDUC., 30, 470 (1953).

Farrington Daniels
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ACS Division of Physical and Inorganic Chemistry Golden Jubilee

The American Chemical Society for its first 30 meetings had only one session at a time. There were no divisions. By the 31st meeting in 1904, in Philadelphia, the society had grown so large and was covering so many specialized fields that the meetings were divided into sections including one for physical chemistry and one for inorganic chemistry. Between 10 and 20 papers were given at most meetings of the Physical Chemistry Section, but at the last one before the divisional merger, there were 43 papers, including papers on electrochemical researches by G. N. Lewis and by Hulett, radioactivity by Boltwood, iodine and potassium iodide by Charles L. Parsons, catalysis in flowing gases by Langmuir, solutions of metals in liquid ammonia by Kraus, hydration of ions by Washburn, and contributions by many others. It was an interesting program, even as viewed by sophisticated chemists half a century later.

On December 30, 1908, at a meeting of the American Chemical Society in Baltimore, plans were drawn up and nominations made for the newly authorized Division of Physical and Inorganic Chemistry. Two days later on January 1, 1909, the first meeting of the Division was held.

In February, 1909, I joined the American Chemical Society as an undergraduate student and in 1910 I presented a paper before the Division of Physical and Inorganic Chemistry. So, I have been privileged to know the Division throughout practically its whole existence.

The success of any organization depends on the men who lead it. The chairmen of this Division are shown here. The gallery is complete. Two-thirds of them are still living. These men were not mere figureheads occupying honorary positions. They were active, producing scientists and since 1920, with only two exceptions, they came to the chairmanship after strenuous service as secretary. All of them would testify to the agonizing times preceding the semiannual, national meetings when just before the deadline the manuscripts pour in.

G. N. Lewis was the chairman of the Division when it was organized. No person has done more than he to advance physical chemistry. He developed chemical thermodynamics, invented the concept of the electron pair and laid the foundations for atomic and molecular structure, and he founded a school of chemistry at the University of California which has produced many creative leaders in physical chemistry.

The membership of the Division for the first year, 1909, must have been around 150. Five years ago it was 1531. In 1958, it was 1900—even after three new divisions had been split from it.

At the 43rd meeting of the American Chemical Society in Minneapolis in 1910, the minutes, as published in the *Journal of the American Chemical Society*, report that a committee was appointed to study the best means of raising $20 to $25 for postage and printing for the division—at present paid for by the secretary. At the 44th meeting, an assessment of $1.00 per member was voted. At the 45th meeting the secretary-treasurer reported that there was $50.93 in the treasury but that only one-third of the members had paid their dues.

There has been a steady rise in the number of papers presented at the Division meetings. As a very rough rule, the number is not too far from being equal to the number of meetings which the American Chemical Society has held since the beginning. At the 42nd meeting in San Francisco in 1910, there were 44 papers, at the 43rd in Minneapolis in 1910, there were 48 papers, at the 77th there were 72 papers, and at the 78th there were 62 papers. Recently there have been about 150 papers at each meeting.

We have looked in at the first meeting when the Division was formed. Three years later at Washington, we find on the program: Langmuir, Hildebrand,

Presented at the Golden Jubilee Celebration, Division of History of Chemistry, at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

G. N. Lewis 1908 | C. H. Herty 1909 | E. C. Franklin 1910 | H. P. Talbot 1911 & 1917 | W. L. Miller 1912 | S. L. Bigelow 1913 & 1918

Bingham, Franklin, Harkins, Kraus, G. N. Lewis, A. A. Noyes, and John Johnson and others contributing papers. The subjects included among others an active form of hydrogen, ammonia compounds, viscosity, rare earths, perchloric acid, ionization theory, electrode potentials, vacuum pumps, and physical-chemical concepts.

At another meeting nineteen years later in Indianapolis in 1931, we read in the symposium on Mathematics in the Service of Chemistry, "The average chemist does not fully realize the tremendous advances that have been made recently through quantum theory and related fields. Advanced mathematics is such a valuable tool in Chemistry now that the alert chemist can no longer remain in ignorance of it."

The program had Randall on Thermodynamics; Fowler on Statistical Mechanics; Dushman on Quantum Mechanics; and Urey on Atomic Structure. Other papers were given by Rodebush on Chemical Equilibria from Band Spectra; by Andrews on Chemical Applications of Raman Spectra; by Mulliken on Electron Quantum Numbers; by Hogness on Strength of Carbon Bonds; by Villars on Band Spectroscopy; by Eyring on Quantum Mechanical Calculation of Heats of Activation; and by H. L. Johnston on Precise Calculation of Specific Heats and Heats of Dissociation to 5000° for 0_2 and NO.

The Division has held over 200 symposia. Of these, 14 have been isolated symposia held at a different time and place than the American Chemical Society meetings. They have been the sole business of the participants for three days, without other distractions. Titles are given here.

Special Symposia

1936	Princeton	Molecular Structure
1937	Cleveland	Less Familiar Elements
1938	Brown	Intermolecular Action
1939	Wisconsin	Kinetics of Gas Reactions
1940	Atlantic City (June)	Tools of Analytical Chemistry
1940	Columbia (December)	Structure of Molecules and Aggregates of Molecules
1941	Ohio State	Recent Developments of the Non-Metals
1946	Northwestern	Color and Electronic Structure of Complex Molecules
1949	Pittsburgh	The Solid State
1950	Minnesota	Anomalies in Reaction Kinetics
1952	Notre Dame	Electron Transfer and Isotopic Reactions
1953	Schenectady	Impurity Phenomena
1954	Yale	Solutions of Electrolytes
1956	Wisconsin	Valency and Chemical Bonding
1958	Northwestern	Mechanisms of Inorganic Reactions in Solution

The titles of symposia at the regular meetings show that the Division has been prompt to help in the development of new discoveries.

Representative Symposia at ACS Meetings

1913	Photochemistry
1915	Industrial Chemistry
1920	Colloids
1921	Contact Catalysis

N. H. Furman 1935
J. W. Williams 1936
H. L. Johnston 1937
H. S. Booth 1938
G. Scatchard 1939
G. F. Smith 1940
J. G. Kirkwood 1941
W. C. Fernelius 1942
R. E. Gibson 1943
O. K. Rice 1944
T. F. Young 1945 & 1946
P. M. Gross 1947

1922 Distillation
1927 Proteins
1928 Atomic Structure and Valence
1929 Chemical Activation by Light and Ionizing Radiations
1931 Mathematics
1935 Chemical Thermodynamics
1936 Deuterium; Quantum Mechanics and Reaction Kinetics
1937 High Polymers; Dipole Moments; Low Temperature Chemistry; Geochemistry
1938 Dropping Mercury Electrodes; Nuclear Chemistry
1940 Tools of Analytical Chemistry; Fluorine Chemistry
1941 Magnetism and Molecular Structure
1942 Hydrogen Bonds; Tracer Isotopes
1943 Free Radicals; Semi-conductors
1946 Co-polymers; Radiation Chemistry
1947 Chemistry of Fission Products; Ion Exchange Separations; Kinetics of Propellants
1948 Transuranium Elements; Organometallic Compounds
1950 Unfamiliar Valence States; High Temperature Reactions; Actinide Elements
1952 Nuclear and Paramagnetic Resonance
1955 Air Pollutants

Philosophies and Innovations of the Division

Believing that there is strength and influence in numbers, the Division has tried over the years to hold together physical and inorganic chemists of widely differing interests. In spite of this it has been a fissioning division, Colloids splitting off in 1927, Microchemistry and Analytical Chemistry in 1940, and Inorganic in 1957. As a matter of fact, within the first year of the marriage between the physical and inorganic divisions, half a century ago, there was agitation for a divorce. A committee was appointed to study the separation. The following year by a 4 to 1 vote, the committee recommended against separation—pointing out that it was difficult to classify and distinguish between the investigations and the investigators in the two fields and suggesting subdivisions in the program when the crowding of the program should become too severe.

There were several later agitations for separation, but the Division stayed together until within a year of its fiftieth anniversary. Now the old division is the Division of Physical Chemistry, and the new Division of Inorganic Chemistry is starting out vigorously and usefully.

The idea of two or more simultaneous sections was not implemented until the meeting at Swampscott, Massachusetts, in 1928, and it has been maintained ever since. Often the Division has run three different meetings simultaneously.

Another innovation, the fixed time schedule, with 15 minutes for each paper, was started by the Division in 1929 at the 77th meeting. In 1930 at the 78th meeting in Minneapolis, 20 minutes each were allowed for the papers. According to the minutes, "the new time schedule was entirely satisfactory and at no time was the program more than 5 minutes behind schedule."

How can we continue to serve the development of physical chemistry and remain strong when there is the urge for greater specialization and more splinter groups? We should always arrange for narrower activities within the larger group, as we have done so

successfully thus far. We ought to be ingenious enough to invent new ways to meet changing conditions in the future. The American Chemical Society with its large influential membership and centralized administration, and yet with its internal specialties and its democracy, has an extraordinary record of achievement. Biological sciences and other professional groups are less effective in science because they have not incorporated the specializations of the small divisions into one large society.

What new problems are likely to arise? Chemical physics is an important and growing field which belongs both to the American Chemical Society and the American Physical Society. The *Journal of Chemical Physics* is an excellent journal, but it has been somewhat of an orphan. In the future perhaps more cooperation can be established between chemists and physicists, just as there is now such fine cooperation between chemists of different interests.

Finally, when new ideas and new laboratory findings are born they will be brought together promptly for information, evaluation, and application by a still stronger and constantly growing Division of Physical Chemistry.

Chairmen of the Division of Physical and Inorganic Chemistry

		Research field	*Laboratory*
1908	G. N. Lewis	Thermodynamics, molecular structure	U. California
1909	Charles H. Herty	Physical Chemistry	North Carolina
1910	Edward C. Franklin	Solutions in liquid ammonia	Stanford
1911	Henry P. Talbot	Analytical chemistry	MIT
1912	W. Lash Miller	Physical chemistry	Toronto
1913	S. L. Bigelow	Capillary action	Michigan
1914	George A. Hulett	Electrochemistry	Princeton
1915	George A. Hulett	Electrochemistry	Princeton
1916	Irving Langmuir	Surface energy; molecular structure	Gen. Electric Co.
1917	Henry P. Talbot	Analytical chemistry	MIT
1918	S. L. Bigelow	Capillary action	Michigan
1919	W. E. Henderson	Physical chemistry	Ohio State
1920	William D. Harkins	Surface phenomena; nuclear structure	Chicago
1921	Harry N. Holmes	Colloids	Oberlin
1922	Samuel E. Sheppard	Photography	Eastman Kodak Co.
1923	Robert E. Wilson	Physical chemistry	Standard Oil Co.
1924	Graham Edgar	Kinetics	Ethyl Corp.
1925	Arthur E. Hill	Phase diagrams	Yale
1926	Harry B. Weiser	Colloids, hydrous oxides	Rice Institute
1927	George S. Forbes	Photochemistry	Harvard
1928	George L. Clark	X-rays	Illinois
1929	Victor K. LaMer	Kinetics; colloids	Columbia
1930	Ward V. Evans	Physical chemistry	Northwestern
1931	Farrington Daniels	Chemical kinetics	Wisconsin
1932	Hobart H. Willard	Analytical chemistry	Michigan
1933	W. Albert Noyes, Jr.	Photochemistry, (editor *JPC* and *JACS*)	Brown (Rochester)
1934	D. H. Andrews	Molecular vibrations	Johns Hopkins
1935	N. Howell Furman	Analytical chemistry	Princeton
1936	John W. Williams	Dipole moments; colloids	Wisconsin
1937	Herrick L. Johnston	Thermodynamics	Ohio State
1938	H. S. Booth	Inorganic chemistry	Western Reserve
1939	George Scatchard	Solutions	MIT
1940	G. Frederick Smith	Inorganic chemistry	Illinois
1941	John G. Kirkwood	Theory of solutions	Cornell (Yale)
1942	W. Conrad Fernelius	Inorganic chemistry	Ohio State (Penn State)
1943	R. E. Gibson	Physical chemistry, propellants	Carnegie Institution (Applied Physics Lab.)
1944	Oscar K. Rice	Kinetics	North Carolina
1945	T. Fraser Young	Thermodynamics, solutions	Chicago
1946	T. Fraser Young	Thermodynamics, solutions	Chicago
1947	Paul M. Gross	Physical chemistry	Duke
1948	Henry Eyring	Kinetics, theory	Princeton (Utah)
1949	Martin Kilpatrick	Kinetics of solutions	Penn. (Ill. Inst. Tech.)
1950	John C. Bailar, Jr.	Inorganic chemistry	Illinois
1951	Milton Burton	Radiation chemistry	Notre Dame
1952	Glenn T. Seaborg	Nuclear chem., transuranium elements	California
1953	Frank A. Long	Physical chemistry; polymers	Cornell
1954	Joseph W. Kennedy	Radiochemistry	Washington Univ.
1955	Frank T. Gucker, Jr.	Calorimetry	Indiana
1956	Pierce W. Selwood	Magnetochemistry	Northwestern
1957	John E. Willard	Radiation chemistry	Wisconsin
1958	David P. Stevenson*	Ion-molecule gas reactions	Shell Dev. Co.
1959	Robert L. Burwell*	Physical-organic chemistry	Northwestern

* Chairmen Division of Physical Chemistry Division; Division of Inorganic Chemistry is separate division.

A ChemEd SYMPOSIUM

Instruction in Inorganic Chemistry

The rebirth of interest in inorganic chemistry and the very substantial progress in research in inorganic areas—both within the past few years—render an examination of instructional practices particularly appropriate at the present time. This is especially true in the light of the physical and theoretical approaches that are in many regions of teaching supplanting the classical, purely descriptive treatments. It is true, also, in the sense that the descriptive areas still retain their importance and require consideration within some general framework that also embraces theory.

In arranging this symposium,[1] therefore, the chairman has asked that contributors give attention to the general themes of "What we should teach" and "How we should teach it." Within these bounds, it has seemed logical to devote attention both to our own approaches and to those that are being used abroad with well-known effectiveness. Accordingly, in the papers that follow, some comparisons between American and European instruction, some new approaches to lecture and laboratory instruction, and some suggestions for implementing the latter are included as expressions of these themes.

Quite obviously, within the limits of such a program it has been impossible to include every current view or perhaps any more than a small sampling of present thought and practice. It is reasonable to hope, however, that the material presented will stimulate others to formulate their own concepts and to bring them to the attention of both teachers and research workers in inorganic chemistry. It is reasonable to hope also that the latter will in turn present their own views since in the light of their experiences and contacts many of them have most certainly been moved to evaluate college and university instruction critically. If inorganic chemistry is to continue its healthy growth and maintain its position of eminence, all inorganic chemists must at all times do everything that can logically keep instruction in inorganic chemistry modern, meaningful, and stimulating.

Therald Moeller, *chairman of symposium*
University of Illinois, Urbana

[1] A symposium sponsored jointly by the Division of Inorganic Chemistry and the Division of Chemical Education at the 134th meeting of the American Chemical Society, Chicago, September, 1958.

Inorganic Chemistry at German Universities

L. F. Audrieth
and **R. J. A. Otto**[1]
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In order to discuss the teaching of inorganic chemistry at German universities and to compare the training received by German students with that received by our students, it is necessary to consider the offerings in this particular field from the point of view of the whole German educational system. Not only are the schools different in their organization, but the German (and continental European) philosophy of education differs from our own concepts in several essential characteristics. First of all, the German system is much more highly selective than our own. Comprehensive examinations are given at stated intervals in order to determine which educational program a youngster is qualified to undertake. Secondly, once that decision has been made, little latitude or choice is allowed the student so far as his curriculum is concerned. The courses of study are prescribed up until he is ready to enter the university. Thirdly, the educational discipline at the pre-university level is rigorous—nothing is left to chance—and is not encumbered by extracurricular activities which play so large a part in our primary, secondary, and college offerings in this country.

Responsibility for all phases and branches of the German educational system, including the universities and the specialized trade and vocational schools, rests with the Ministry of Culture in each of the ten states that comprise the West German Republic. Each

[1] Present address: Chemisches Institut der Universität, Heidelberg, Germany.

state enjoys complete autonomy, but by appropriate interstate arrangements coordinates its requirements with those of the other nine states. The curricula in the various schools, including private schools, and the minimum requirements in the various subjects, are set up by the respective state ministries of culture and are obligatory for all schools, except the universities.

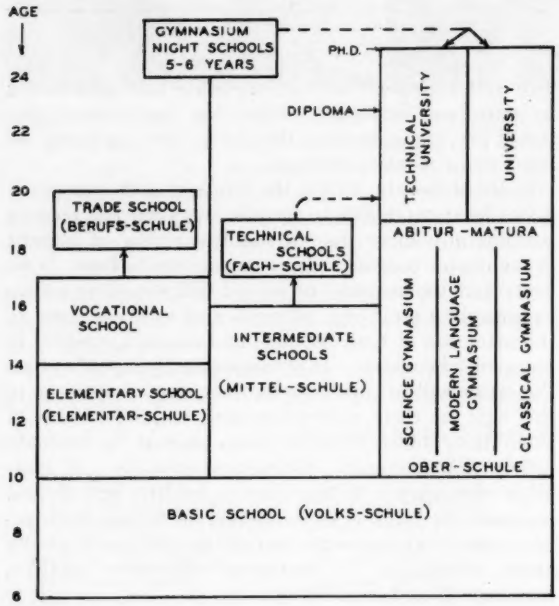

Figure 1.

Practically all teachers are state employees—suffice it to add parenthetically that teaching is a respected profession. Communities are responsible only for the erection, care, and maintenance of school buildings. School attendance, even though it may in later years be part time, is required of all children from the ages of six to seventeen. Where possible, separate schools are maintained for boys and girls, with men and women teachers, respectively.

In its broadest aspects the organization of the German educational system is depicted in the figure. All youngsters attend basic school (Volks-schule) for four years. A uniform examination covering essentially writing, reading, and arithmetic is then given to determine the future educational program of the ten-to-eleven-year-old youngsters. The less qualified students go on to four years of elementary school, followed by three to four years of vocational training, the latter frequently consisting of apprentice or industrial in-service training, leading to certification as a qualified vocational worker. Such an individual may subsequently attend a more advanced, full-time trade school for at least two years leading to certification as a skilled or master-workman.

The intermediate school (Mittel-schule) is a public school which is more rigorous in its general requirements, but less so than the gymnasium. Only one foreign language is required, but courses in German language and literature, history, geography, mathematics, and general science are offered for the six-year period. The student may then proceed to a two-year technical school for specialized training. Thus, for instance, he may attend a school for the training of chemical technicians, such as the Fresenius School in Wiesbaden. Courses are given in general, analytical, organic, and physical chemistry, in chemical technology, and in bacteriology—but the real emphasis is devoted to laboratory training in each of these fields. Except for lectures and class work, the student is required to spend all of his time in the laboratory from 8:00-12:00 and 1:00-5:00 for five and one-half days per week for four semesters. After completing the required subject and "practical laboratory" examinations, he is qualified as a Chemotechniker, that is, a chemical technician. However, he is not a professional chemist any more than a medical technician can call himself an MD in this country. It is possible for a graduate of a technical school to enter the Technical University for professional training in his particular technical field and thus achieve professional status.

The normal route to the university is through the gymnasium. If the youngster, after four years of basic school, has done well in the classification examinations, he may be sent to an "ober-schule," but note that the choice as to the type of gymnasium is a decision which is left to the discretion and the personal desires of the parents. The three major types of gymnasia represent schools with slightly different concentration on the foreign language, science, and mathematics requirements. This nine-year school (eight years in Austria) places particular emphasis on German language and literature (both written and oral expression), mathematics (at least through calculus), scientific literacy (biological, physical, and earth sciences), foreign languages, history, and geography—with courses in art, music, and religion also required. Physical education in the form of gymnastics and individual sports is emphasized rather than team sports. The major differences with respect to foreign languages, mathematics, and science requirements are reflected in Table 1.

There is practically no choice with respect to "electives." The whole curriculum is prescribed. Failure in one of the major courses in any one year, or in two of the minor courses, requires repetition of all courses offered during that year. Classes are held six days per

Table 1. Typical Curricular Differences in the German Gymnasium

Gymnasium	Courses	Years	Hours/week
Classical	Latin	9	7–5
	English	6	4–3
	Greek	5	5
	Mathematics	9	5–3
	Physics	5	2
	Chemistry	4	2
Modern language[a]	Latin	9	7–4
	English	6	4–3
	French	5	5–4
	or		
	English	9	6–3
	Latin or French	6	5–4
	French or Latin	4	4–3
Science	English	9	6–3
	French	6	5–3
	Mathematics	9	5–4
	Physics	5	3–2
	Chemistry	4	3

[a] Mathematics, physics, and chemistry requirements are the same as in the classical gymnasium.

week from 8:00 until 1:00. Homework and home study assignments keep the average youngster busy every day for an additional two to three hours. Written and oral examinations and so-called "home examinations" are frequent (monthly and at the end of the semester). The comprehensive examinations following the ninth year cover six-hour written and essay examinations in German language and literature, mathematics, foreign languages, and the physical sciences. Oral or written examinations are also required in other subjects. Successful completion of these "abitur" (matura) examinations is a requirement for admission to a university.

From the point of view of scientific training, several significant features are discernible: (a) rigorous mathematical training, (b) achievement of general scientific literacy, and (c) ability to handle foreign languages. Physics is normally introduced before chemistry, since generalizations with respect to physical phenomena can best be expressed mathematically. Chemistry offerings cover general and inorganic chemistry, organic chemistry, and elementary physical chemistry with emphasis on the descriptive aspects of the subject in its relationship to the impact of chemistry on everyday life and living. Laboratory work is optional.

The student has now "matured" after a rigorous educational program through four years of basic school and nine years of the gymnasium. He is now ready to specialize in some particular field of knowledge. He may attend a technical university (Technische Hochschule) or the university. The differences between the two types of universities have gradually become less pronounced and broadly rest on the distribution of "faculties" in which specialization is possible. The universities consist of five faculties (Philosophy, Theology, Medicine, Law, Natural Sciences); the technical universities are limited to faculties of Philosophy and the Natural Sciences. The universities represent the outgrowth of long-established scholastic and humanistic traditions based upon a concept of academic freedom as applied to research, instruction, and learning; the technical institutes are more recent in their development and were founded during the 19th and 20th centuries as a result of progress, and need for training, in the applied sciences and technology.

Study of chemistry at the university may lead either to the title of Diplom-Chemiker, or, with approximately two years of additional effort, to the doctorate (Dr. rerum naturalium). The student is given wide latitude with respect to attendance at lectures; only a few general survey courses are required. Fees are charged for attendance at lectures. The "mature" student may decide to master the theoretical as well as the descriptive material by "self-study"—and this is not infrequently the case. However, all students majoring in chemistry are required to complete prescribed laboratory courses (praktika) in the three major branches of chemistry—inorganic (including analytical), organic, and physical chemistry—before a minor research problem is undertaken in some special field. The student must also complete during this time laboratory praktika in one or two related scientific fields which constitute areas of lesser specialization. Actually, it is not until the "Diplom-arbeit" is undertaken that the student indicates special interest in some branch of chemistry. After completion of what amounts essentially to a master's thesis, a student must pass successfully oral examinations in the three branches of chemistry and in the one or two scientific areas which represent his minor subjects. In some universities these examinations precede the "diplom-arbeit." He is then a Diplom-Chemiker and may accept an industrial position as a professional chemist, or he may take written examinations to qualify for a position as an Ober-schul-lehrer or continue for the doctorate.

Instruction in Inorganic Chemistry

It has already been implied that separate chairs in inorganic and in analytical chemistry normally do not exist at German universities. Consequently, the first praktikum in inorganic chemistry covers (a) qualitative analysis, (b) quantitative analysis, and (c) inorganic preparations. The more advanced praktikum in inorganic chemistry (frequently taken after praktika in physical chemistry and organic chemistry) is designed to familiarize the student with advanced techniques and more difficult inorganic syntheses from the modern literature. The "advanced techniques" vary from one university to the next and frequently reflect the specific research interests of the professors in charge of such a course.

Laboratory space is at a premium in most German universities. The student must therefore complete his laboratory work in a reasonable time or forfeit his place to someone who may be waiting to begin the praktikum. Consequently, the student devotes all of his free time to laboratory work. Thus, the laboratories at Heidelberg are open Monday to Friday from 8:00 A.M. to 6:00 P.M., while the university is in session.

Preliminary experiments and textbook study together with an oral test by the assistant in charge precede laboratory work on each group of unknowns in qualitative and quantitative analysis. The course content and unknown requirements for a typical laboratory course in qualitative analysis are outlined in Table 2. It may

Table 2. Laboratory Course in Qualitative Analysis (University of Innsbruck)

1.	Simple anions (2)[a]
2.	Alkali and alkaline earth elements (4)
3.	Ammonium sulfide group (4)
4.	HCl and H_2S groups (4)
5.	All cations (4)
6.	Less common anions (4)
7.	Solids—salts, salt mixtures, ores, alloys (6)
8.	Rare elements—cationic and anionic species derived from elements—Tl, Se, Te, Mo, W, Be, V, N, Zr, Ti, Ta, Nb (4 complete analyses)
9.	Practical laboratory examination—2 days
10.	Oral exam covering all of qualitative analysis

[a] Figures in parentheses indicate number of required analyses.

be of interest to note that simple anions are studied first, that the order of issuance of unknowns does not follow the systematic scheme of qualitative analysis, and that some familiarity with the less common elements or less familiar oxidation states of commoner elements is developed. The laboratory work in quantitative analysis (with number of required analyses given in parentheses) covers gravimetric determinations (6) and practical work in acidimetry (6), oxidimetry (5), iodimetry (4), precipitation reactions (4), com-

plexometric methods (1), and electrolytic procedures (2). Both quantitative and qualitative analyses of a silicate mineral, a non-silicate mineral, two alloys (containing three to four components), and a steel alloy for trace constituents, followed by an oral examination, complete the quantitative work. Six to ten typical inorganic preparations are then assigned. The laboratory record for each must contain information concerning literature references, alternative procedures, experimental data, and physical and chemical properties. Laboratory work in qualitative analysis, quantitative analysis, and inorganic preparations, together with prescribed oral examinations, constitute the first inorganic praktikum. A laboratory course of this type is required of all chemistry majors at all German universities.

The more advanced praktikum in inorganic chemistry varies among universities. Ten more difficult inorganic syntheses are required. Frequently, these are assigned to verify or check procedures published in the modern literature or to afford experience in special techniques applicable to preparative inorganic chemistry.

Formal lecture offerings vary among universities. They may frequently reflect the special research interests of members of an academic staff. It was once customary to travel from one university to another to audit the lectures of this or that noted or distinguished professor in his special field. This is still done to some extent but not so frequently as in the pre-World War I years. Certification at any one university with respect to either laboratory work or attendance at lectures is acceptable at all other institutions of higher learning within any one country and usually elsewhere in continental Europe.

Doctorate work represents the ultimate in specialization. At least two years of effort are normally required for completion of the experimental work and presentation of a thesis. The final oral doctorate examination is comprehensive in character, covering not only the thesis results but also the competency of the candidate in all three branches of chemistry and in the related scientific areas representing fields of lesser specialization.

It seems not inappropriate to conclude this discussion by pointing out that inorganic research in Germany is strongly concentrated on synthetic problems. The leading inorganic chemists of Germany have emphasized the experimental approach and used instrumental and physico-chemical methods to expand tremendously our background and knowledge of descriptive inorganic chemistry.

Acknowledgment

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Inorganic Chemistry Training in British Universities

The history of chemistry teaching in the United States has included relatively strong emphasis on descriptive inorganic chemistry, analytical chemistry, physical chemistry, and organic chemistry. In the case of organic chemistry, following a classical approach in earlier years, recent years have seen the development of a relatively greater emphasis on physical-organic chemistry. Although there has been an increasing trend to study inorganic systems and phenomena more intensively from a physical-chemical point of view, the extent of such study and the degree to which it has been incorporated in chemistry curricula in this country is still limited, especially by comparison with the trend in some parts of the United Kingdom and on the continent. In the meantime, the great importance of teaching and research in this area has become apparent in connection with the development of such subjects as nuclear physics and chemistry and nuclear engineering, which deal with a wide variety of inorganic materials and systems. It would seem that there must be a much stronger development of these aspects of inorganic chemistry than has been true in the past and that they should have a more prominent place in future college and university chemistry curricula.

Among nine of the leading English and Scottish chemistry departments that were visited, and from a more limited sampling of those at continental universities, a fairly consistent pattern appears. Those apparently having the greatest success in the development as centers of inorganic chemistry, as measured by such criteria as the publications and reputations of the

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department members and the ability which the department has to attract inorganic students both at the undergraduate and graduate levels, seem to have the following elements in common: of the total time available for chemistry, both in lectures and laboratories, approximately a third tends to be devoted to inorganic (including analytical), a third to physical, and the remaining third to organic. At all levels of inorganic instruction an effort is made to integrate the theoretical concepts of chemistry with the descriptive material. It should be pointed out that often the structural inorganic courses overlap what is commonly called a physical chemistry course here. In addition, laboratory courses are being modified by placing greater emphasis on preparative inorganic which is, in turn, integrated with the analytical work.

The integration of the theoretical and descriptive material of necessity takes different forms at different places. At Cambridge, which has an outstanding theoretical chemistry department, eminent theoreticians give the lectures in theoretical chemistry which are designed to complement simultaneously offered organic and inorganic lectures. As an example, the theoretical discussion of the bonding in ferrocene-type compounds is presented about the same time that the descriptive chemistry of ferrocene and similar compounds is dealt with in the inorganic course. Similarly, on the organic side, the structure of benzene is discussed by the theoreticians at about the time that the properties of aromatic compounds are being considered in the organic course. The whole emphasis in the teaching of the theoretical chemistry is in the direction of a qualitative understanding of the most recent theoretical concepts as applied to numerous specific examples. At the same time every effort is made by the inorganic instructors at this particular level to explain structural problems in a manner consistent with modern theory. The result is that most of the students learn to think qualitatively in terms of such concepts as the ligand field theory and molecular orbitals. This is made easier of accomplishment by the full use of the tutorial system at institutions such as Oxford and Cambridge. In a somewhat different manner a similar end is achieved at such larger institutions as Imperial College and University College of the University of London and at some of the smaller universities such as Nottingham and Southampton, primarily by having the content of the inorganic courses arranged so that the inorganic instructor presents the rudiments of theory needed at appropriate times along with the descriptive material. At University College, in particular, there is very good integration in the presentation of chemistry as a broad discipline including both its experimental and theoretical aspects. The organic, inorganic, theoretical, and physical aspects of a chemist's training are well integrated there into one comprehensive chemistry program.

New Approaches to Inorganic Laboratory Training

Perhaps the most significant developments recently in the handling of inorganic teaching in Great Britain have been those relating to the laboratory work. Much time and thought are being devoted to the means for conveying to the student an appreciation of the diverse facinating problems open to him in the field of inorganic chemistry. At Cambridge, to date, the modifications in the inorganic and analytical laboratory work have been restricted to the introduction of a limited number of advanced inorganic preparations and an attempt to prevent repetition of school laboratory work by carrying out the qualitative and quantitative procedures on less known elements and for cases involving less common valence states. However, the incorporation of considerably more preparative work is contemplated in the near future. Every effort has been made to reduce the time necessary for each individual experiment. Micro techniques are used when feasible and semiautomatic balances are available to all students. The time devoted to inorganic and analytical in the laboratory there, however, is somewhat less than that spent on organic or physical. At Oxford, there has been a somewhat greater integration of the preparative and analytical work in the laboratory, and also there has been considerable emphasis placed on physical-inorganic techniques. The latter include such experiments as the determination of the stability of a complex, partition experiments, and ion exchange separations. The laboratory time at Oxford is about evenly distributed among inorganic, physical, and organic courses.

A fairly complete revision of the inorganic laboratory work has been undertaken by Imperial College and University College of the University of London during the last several years. At University College, for example, in the first laboratory course a period of time is devoted to analytical techniques such as acid-base titrations, oxidation-reduction titrations, and simple gravimetric procedures using semiautomatic balances. The students are then expected to prepare carefully an analytical sample of a compound such as potassium aluminum oxalate and to analyze their preparation. In this case they would analyze for oxalate by two different methods and for the metals also by two different methods. Following this, they have test-tube-type experiments concerning the less common elements of the periodic table such as cerium, titanium, zirconium, and thorium. In the physical chemistry laboratory considerable time is devoted at an early stage to instrumental techniques which could be of use to the inorganic chemist. These are taken advantage of in the more advanced inorganic laboratory where the students prepare known but unusual compounds, followed by a check analysis and a study of their chemical and physical properties. The aim is to provide practice in more advanced preparative techniques in inorganic chemistry, such as those involving the absence of oxygen and/or moisture, and practice in the application of physical techniques to inorganic chemistry, such as molecular weight determinations, conductivity measurements, magnetic moment evaluations, and potentiometric titrations. A typical example could be the preparation of cuprous complexes of diphenylmethylarsine by a method selected by the student after searching the literature. Then an analysis would be carried out for copper and halogen, and a determination would be made of the magnetic moment, molecular weight, and conductivity in nitrobenzene. A certain measure of the success of such a program when well presented can be gained from the very high proportion of students who wish to continue into graduate school in inorganic chemistry at University College. At Imperial College

the program has only just commenced so it is more difficult to evaluate. Here, there appears to be a somewhat greater emphasis placed on newer analytical techniques such as ion exchange and paper chromatography, but again there is a very high proportion of the time devoted to interesting inorganic preparations, their analysis, and the examination of their physical properties. Of the smaller universities, both Nottingham and Southampton are having considerable success in their inorganic laboratory work along lines somewhat similar to those at University College.

Similar trends in curriculum organization are evident in King's College of Durham University, at Newcastle, and at Scottish universities such as Edinburgh and Glasgow, but apparently they have not taken place to the same degree as in the English institutions cited.

In summary, to one familiar with the methods of teaching and the handling of research in American institutions, there appears to be emerging a somewhat modified concept in dealing with chemistry as one of the basic scientific disciplines in England and Scotland, some aspects of which might profitably be applied to our own situation. This is characterized by an integrated experimental and theoretical approach ranging broadly from a wide descriptive background coupled with intensive experimental laboratory exercises and a modern theoretical treatment of the interpretation of structure. This results in high stimulation of student interest together with strong motivation to pursue a research and investigative career. This approach appears to be equally applicable in small or large institutions.

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A Meaningful Inorganic Chemistry Course

Most students gain their impression of inorganic chemistry from their contact with it in high school chemistry and in freshman chemistry. Chemistry majors and a few other students will, in addition, take one or more advanced courses in which they will broaden their view of inorganic chemistry. Do these courses give the student any idea of what inorganic chemistry is really about? Unfortunately, there are some high school and freshman chemistry courses in which inorganic chemistry is presented as a collection of relatively unrelated facts, and it is not surprising that a typical student reaction is that chemistry is essentially a memory course with little rhyme or reason to the many facts which are encountered.

To consider whether such courses can properly equip a student who plans to work in chemistry or whether such courses can give a non-chemistry major some comprehension of what chemistry is about, consider for a moment what an inorganic chemist tries to do. I would state that the ultimate aim of chemists is to possess the ability to predict the chemical behavior of any conceivable system under all conceivable conditions. The combinations of materials and conditions in which one could be interested are astronomical. It is not conceivable that one could ever hope to obtain the desired chemical information from experiment alone. One must have means of interpolating between experimental points and extrapolating beyond them to obtain all the information that one needs for predicting chemical behavior.

In principle, quantum theory, starting from first principles, can predict chemical behavior with as high a degree of accuracy as might be desired. However, it seems very unlikely that a completely deductive approach to chemistry will be adequate in the lifetime of the present chemistry students. One is forced to set up various approximate theories to represent the chemical interactions between atoms in a molecule or between different molecules. The usual approach of an inorganic chemist is a combination of inductive and deductive steps. He will examine experimental data to look for relationships which can be represented by a theory of interactions between atoms and molecules. The chemist often finds it useful to express interactions between even microscopic atoms or molecules in terms of a concrete classical model. He will then attempt to calculate the expected behavior on the basis of this model. Upon comparison of the predictions with observations, he will then return to his model and refine it until he obtains sufficient agreement with the known results. The ultimate refinement requires conformity with quantum mechanics. Once a model is obtained which agrees with the known results, it may then be used to interpolate with reasonable confidence to predict chemical behavior under conditions not too far removed from those which have been studied. Through use of mathematics, the results of the model can be expressed in compact analytical form. In addition, one may then attempt to extrapolate on the basis of this model to predict behavior under conditions

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which have not yet been studied experimentally.

From this point of view, an experiment is not carried out in order to obtain results for a specific system, but it is carried out to test the adequacy of a theory to predict chemical behavior over a wide range of conditions. Each experiment, if properly designed, thus gives us information about what would happen in a large number of other experiments. When experiments are designed to test theories, important new discoveries which indicate unexpected interactions are immediately apparent. When experiments are carried out in a random manner outside the context of a theory, one could encounter important observations and not be aware of their novel importance. The emphasis in inorganic research should be on the design of experiments which will severely test the ability of various theories to extrapolate chemical behavior beyond the region which has been studied experimentally in the past.

This emphasis must also be reflected in the presentation of inorganic chemistry in courses not only at the graduate level but at undergraduate and even high school levels. Chemistry must not be presented as a collection of apparently unrelated observations. The relationships between chemical observations should be emphasized, and the use of theory for correlating data and extrapolating data should be demonstrated in courses. The need for advanced mathematics to express the complex functional relationship in chemical systems should also be emphasized. One of the most important aids in correlating data is, of course, the periodic table (*1*) and the periodicity of electronic structure. The correlation of chemical behavior to position in the periodic table (*1*) and, therefore, to size (*2*) and electronic structures of the atoms and to the nature of the bonding (*3*) between the atoms is of utmost importance as a framework upon which inorganic chemical facts can be presented.

This approach places great emphasis upon models which describe chemical bonding such as a model based on covalent bonding or sharing of electron pairs or the ionic model which describes bonding in terms of coulombic interaction and similar concepts. The importance of providing a mathematical description of these models must be emphasized. In elementary courses these models should be presented in their simplest form so that the student can readily grasp the concept represented by the model and so that he can use the models easily for making predictions. One often hears objections to the presentation of simple models in that their range of validity is often not great, and the student soon finds instances where the model is inadequate. It is not necessary to apologize for the inadequacy of these simple models. It is very important for the student to realize that the models that the chemist uses to represent chemical interactions are approximations and, therefore, will be limited in their application. The chemist's main activity is directed toward determining the range of application of these models and what must be done to modify them to allow them to be usable over an even wider range of conditions.

As an example of some simple concepts that can be used to correlate chemical behavior, one can point to the formation of ammonia complexes by various cations. One can show the correlation between electronic structure and tendency to form strong ammonia complexes by pointing out that cations with completed octets have very little tendency to form ammonia complexes whereas those with incomplete octets have strong tendencies to share the electron pair donated by the ammonia molecule to form strong complexes. In the light of such a concept the student can readily make predictions about the strength of ammonia complexes of various cations that he might encounter. Having once developed this picture, one can easily move to related ones.

For example, in answer to the question as to why sulfides of cations with completed octets, such as alkali, alkaline earth, and aluminum cations, are soluble in water whereas sulfides of cations with incompleted octets are insoluble in water, one can draw upon the same concept again. One can point out that a sulfide ion can donate a pair of electrons just as the ammonia molecule can. The sulfides of elements such as copper, mercury, and zinc, which form strong ammonia complexes, would be expected to have abnormally stable solid sulfides because of the extra interaction between atoms due to the sharing of the electron pair.

Comparing cations with comparable size from various parts of the periodic table, one would expect the same solubility on the basis of a purely ionic model. If one then modifies the ionic model to take into account the sharing of an electron pair, one can see that sulfur would be expected to give up or share its electrons more readily than oxygen due to the greater distance of the electrons from the center of the sulfur ion. Thus one would predict that in competition with an aqueous solution the solid sulfides of those elements with incompleted octets would be much more stable, or less soluble. With relatively simple concepts, one can relate the strength of ammonia complexes and the solubility of sulfides as a function of position in the periodic table. One can extend this treatment to many other properties.

With relatively little preparation and on the basis of a relatively few simple models, it can be demonstrated to the student that he can correlate and predict a large number of chemical observations and that, therefore, these observations need not be memorized. With the knowledge of the periodic table and the variation of size and electronic structure across the table, the student can, through the use of simple bonding theories, predict chemical behavior with a considerable degree of success. It may be pointed out to the student that often it is necessary to use several bonding models to represent adequately a large body of data with the applicability of the models often overlapping. Many students attribute too much reality to the models themselves; the experimental observations are the fundamental reality. There is no inconsistency in having two apparently unrelated models being used simultaneously. One may sometimes attempt to correlate chemical behavior in terms of an ionic model as a starting point or in terms of a covalent model as a starting point. Each of these models will in general be crude approximations which must be modified considerably to represent the observations. Using either starting model it is possible, through use of often complex mathematical transformations, to modify them to represent the same behavior in many cases. The choice of a given starting model will depend more

often upon convenience, rather than upon any fundamental advantage. Clearly the model which yields the best initial approximation to the observed facts is the most convenient starting point. Thus the ionic model is the most convenient starting model to use when dealing with cations on the left-hand side of the periodic table, such as the alkali and alkaline earth cations, whereas a covalent model is the most convenient when one is dealing with elements on the right-hand side.

Utility of the Ionic Model

Because of its simplicity, the ionic model is a particularly useful one for predicting chemical behavior (*4–9*). The student has readily available the two important parameters, namely charge of the ions and their sizes, so that he may readily carry out calculations to predict varying stabilities across the periodic table. A complete treatment considering polarization, crystal field theory, and other interactions requires mastery of quite advanced mathematics, but many of the main features can be demonstrated in elementary courses with simpler treatments.

Thus a very crude ionic model can be used to predict variations of acid or base strengths across the periodic table. For example, in the fifth group from nitrogen to bismuth such a model correctly predicts that the acid strengths of the hydroxides of a given oxidation state decrease from nitrogen to bismuth whereas the base strengths increase from nitrogen to bismuth. As the

Table 1

ΔH°_{298} for $1/x\ MF_x(s) = 1/x\ M(s) + {}^1/_2\ F_2(g)$ in kcal per gram-atom of fluorine

LiF 146.3	BeF_2 118.	
NaF 136.0	MgF_2 131.8	AlF_3 117.0
KF 134.5	CaF_2 145.2	
RbF 131.3	SrF_2 145.2	
CsF 126.9	BaF_2 143.5	

cation size increases, the proton on the hydroxide group is less strongly repelled and the hydroxide ion is less strongly attracted. The simplest model is, of course, quite inadequate for quantitative predictions in this part of the periodic table where the representation in terms of ionic models is far from adequate. However, this crude model is still quite useful in correlating the trends and is a valuable one to demonstrate to the students. It may be extended to predict that stannic hydroxide will be a weaker base and a stronger acid than stannous hydroxide and to predict that the stannites will be more hydrolyzed than the thio-stannites. Quite a large body of chemical facts can be readily correlated to even the crudest ionic model and thus give the student some basis for predicting chemical behavior without the need for memorizing a large body of specific facts.

Stability of Halides and Oxides

Another interesting application of the ionic model is to the explanation of trends of stability across the periodic table. In Table 1 are presented the heats of formation (enthalpies of dissociation) per gram-atom of

Table 2

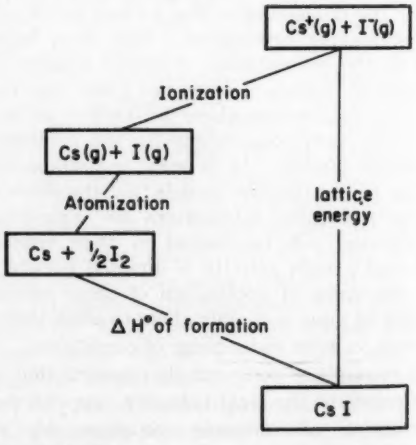
ΔH°_{298} for $1/x\ MI_x(s) = 1/x\ M(s) + {}^1/_2\ I_2(s)$ in kcal per gram-atom of iodine

LiI 64.8	BeI_2 25.3		
NaI 68.8	MgI_2 43.0	AlI_3 24.7	
KI 78.3	CaI_2 63.9		TiI_4 26.0
RbI 78.5	SrI_2 67.8	YI_3 47.7	ZrI_4 33.0
CsI 80.5	BaI_2 72.0	LaI_3 53.1	

halogen of the fluorides of a number of the metals (*10*). The heats are given for the reaction resulting in the formation of the same number of moles of fluorine gas in every instance to insure that the standard entropy change is relatively independent of the metal involved. Thus the heat of reaction will be the determining factor in predicting trends in the standard free energy of reaction and therefore in the logarithm of the equilibrium constant. One notes that the variation of the heats of formation per gram-atom of halogen is proportional to the variation of the logarithm of the equilibrium partial pressure of halogen resulting from decomposition of the halide. It will be noted that for the alkali metal compounds, lithium fluoride is the most stable and cesium fluoride is the least stable.

Table 2 gives the corresponding data for the iodides. Here one finds that cesium iodide is more stable than lithium iodide. The variation in these heats represents the variation in chemical behavior under equilibrium conditions. If one examines the trends among the other elements in the periodic table, there seem to be unexplained variations of stability. If one re-examines these variations in terms of the Born-Haber cycle, one can present a very simple explanation which allows one to predict variation of stability of a very large number of compounds.

The Born-Haber cycle is represented in the figure, using CsI as an example. The over-all process of combination of the elements to the compound is broken up into a number of elementary steps, such as the atomization of the elements and subsequent ionization to produce the gaseous ions which then combine to form the solid lattice. In this last step where the gaseous



Born-Haber cycle for CsI.

ions are brought together to their equilibrium distance in the solid lattice, the heat liberated will be determined by the charges of the ions and the distance to which they can approach one another. For the alkali elements, the charges are all the same. For the iodides the inter-ionic distances are largely fixed by the radius of the iodide ion. There is little variation in the interionic distance going from lithium iodide to cesium iodide and therefore little variation in the lattice energy—the energy liberated upon combination of the gaseous ions. Since there is little variation in this step, the variation in the heats of formation must be fixed by the variation of the heats of sublimation of the metals and the variation of the ionization potentials of the gaseous metallic atoms. In going from lithium to cesium the energy required to produce gaseous ions decreases rather rapidly and thus accounts for the higher stability of the cesium iodide compared to the lithium iodide.

If one now examines the corresponding steps for the fluorides, one finds that the lattice energies vary greatly because the size of the fluoride ion is not so great compared to the cations as was the case for the iodide. Since the fluoride ion is comparable to the size of the cations, there will be a very large percentage change in the interionic distance in going from lithium fluoride to cesium fluoride, and lithium fluoride will have a much greater lattice energy than cesium fluoride. This trend in lattice energy is more than enough to offset the variation in heat of sublimation and ionization potential of the alkali elements; thus lithium fluoride is more stable than cesium fluoride. In terms of this simple model, what seems to be a quite anomalous behavior is readily explained and the variation of the stability of iodides is correlated to the variation of stability of fluorides.

This type of treatment can be greatly extended. As a general statement one can say that the heats of sublimation and the ionization potentials of the metals will be the dominating factors in determining the variation of stability of the compounds when the anions are large compared to the cations, whereas the variation in lattice energies will be the dominating factor when the size of the anions is comparable to that of the cations. If one re-examines the variation of stability of fluorides across the periodic table, one sees that in the second group the beryllium ion is so small compared even to fluoride ion that there is increase in stability going from beryllium to magnesium to calcium. Eventually the size of the cation becomes large enough compared to the fluoride, and the stability decreases upon further increase in size of cation. The third group cations are so small that there is a continuous increase in stability from the smallest cation to the largest cation.

If one were to examine similar tables representing heats of formation per gram-atom of non-metal of metal oxides, sulfides, and many other types of compounds, one would find a similar behavior, namely that the compounds in which the anions are very large compared to the cations will show the highest stability in the lower left-hand corner of the periodic table with the stability decreasing as one goes upward or to the right. Compounds containing an anion comparable in size to the cation will show a ridge of stability extending from lithium down to thorium, in the case of the fluorides and oxides, with stability falling off in either direction. In Table 3 are presented the heats of formation per gram-atom of oxygen for oxides (*11*) to illustrate the validity of these predictions.

Table 3

ΔH°_{298} for $1/x\ MO_x(s) = 1/x\ M(s) + {}^1/_2\ O_2(g)$ in kcal per gram-atom of oxygen

Li_2O 142.4	BeO 143.1	B_2O_3 101.8		
Na_2O 99.4	MgO 143.8	Al_2O_3 133.5	SiO_2 105.0	P_2O_5 72.0
K_2O 86.4	CaO 151.8	Sc_2O_3 137.0	TiO_2 112.8	V_2O_5 74.6
Rb_2O 79.0	SrO 141.1	Y_2O_3 140.0	ZrO_2 130.8	Nb_2O_5 91.0
Cs_2O 76.0	BaO 133.5	La_2O_3 142.8	HfO_2 133.0	Ta_2O_5 97.8
			ThO_2 146.6	

Prediction of Solubilities

In terms of this picture, then, one has a ready answer to the student who asks, "Why do the solubilities of the sulfates of the alkaline earths decrease as we go from beryllium to radium, whereas the solubilities of the hydroxides or of the fluorides show the reverse trend?" The solubility process involves a competition for the cations between the anions of the solid and the water of the solution. Thus such processes as the atomization and ionization of the elements can be omitted, and the Born-Haber cycle may be simplified to a comparison of the lattice energies directly with one another and with the hydration energies of the ions. For carbonates and sulfates, compounds with large anions, the lattice energy shows little variation with size of the cation. On the other hand, for compounds like the hydroxides and fluorides, which contain small anions, the variation of lattice energy will be a large factor which will tend to reduce the stabilities of the solids as the size of the cation increases. The complete application of this model also involves the treatment of the aqueous solution in terms of the interaction between the cation and a water dipole. Water corresponds in size to a small anion like F^- or OH^-, and hydration energies decrease from Be^{++} to Ra^{++}. Because the water dipole has a smaller effective charge than an ion in a solid lattice, the variation in hydration energies is not so large as the lattice energy variations for solid fluorides or oxides.

The general prediction of this model would be that the solubilities of carbonates and sulfates should decrease with increasing cation size due to decreasing hydration energy in contrast to little change in lattice energy. In going from beryllium to barium, the cation in aqueous solution becomes less stable compared to the carbonate or sulfate lattice, which results in a rapid decrease in solubility. On the other hand, lattice energies of fluorides and hydroxides show the same trend with cation size as the hydration energy, with the rate of change of hydration energy being the smaller. From this one would predict that the solubilities of the fluorides and hydroxides should decrease with decreasing cation size until the cation has become quite small compared to even fluoride and hydroxide ions.

One can then generalize that for a compound of the alkaline earth elements in which the cation is associated

with a large anion, one would predict that the solubility would decrease rapidly on going from beryllium to barium. On the other hand, for alkaline earth compounds containing anions which are comparable to the size of the cations, one would predict that there would actually be a reverse trend in that the barium or radium compounds would be more soluble than the compounds of the smaller alkaline earth elements.

There are, of course, many other models that the chemist uses for correlating chemical behavior, but the ionic model is a particularly useful one for elementary courses in that the sizes of the parameters are readily obvious and the computations are quite simple to make if polarization effects are ignored. I believe that good use of it can be made at the freshman chemistry level. The essential features of the Born-Haber cycle can often be used even though one does not go through the details of the entire process. When one is dealing with a range of compounds where only one term predominates, the variation can be described in terms of that one term, for example, the variation of ionization potential.

Correlation and Prediction

What can the student gain from considerations of the above type? The non-science major will gain an insight into the methods by which scientists have gained such powerful control over our environment. By searching for relationships between experimental chemical observations, chemists have gained the ability to predict chemical behavior. The chemistry major will gain a feeling of great power from the ability that he has developed to predict chemical behavior. After he has attained a mastery of thermodynamics, he will look back at the number for magnesium fluoride in Table 2 and, in his mind's eye, he will not see a number. He will see solubilities, hydrolyses, disproportionations, vapor pressures, oxidations, heats of solution, and the great assemblage of equilibrium and calorimetric measurements involving magnesium fluoride which have been carried out in the last century. He will not only see all the many chemical observations that are summarized in that number, he will know that the numbers in the tables, together with their associated entropy and heat capacity values, put at his finger tips not only all the observations of the past on chemical equilbria, but also the ability to calculate behavior under conditions intermediate between those of the experimental observations and those even extrapolated beyond to not yet attained conditions. His understanding of the relationships between the known heats of formation gives him the ability to estimate heats of formation for compounds which have not yet been studied or even prepared; so, in his mind he sees not only the summary of the known observations and predictable observations of the well-known oxides and halides but also the chemistry of the sulfides, the nitrides, and the phosphides, the carbonates, and sulfates. He has learned that no chemical observations are isolated and unrelated to other observations. From the chemical behavior of fluorides, he can predict the chemical behavior of seemingly unrelated sulfates.

As he looks again at the numbers in the tables, he does not see just numbers, he sees chemical behavior in the stars and comets. He sees chemical reactions in rocket exhausts, fused salts, aqueous solutions, and liquid ammonia. He sees more details of chemical behavior than even an IBM 704 can memorize. He knows that all this information is available to him even though he has not yet examined the details of this information, for he has learned a general method of approach that is not limited to the few examples used to illustrate the general procedure. In the process of learning how to correlate data for all the elements, the student will normally learn thoroughly the chemical behavior of only a few illustrative elements. But the expansion of his knowledge has not been limited to the facts relating to these few elements. Through mastery of the general approach outlined above, he can make each fact reap a manifold harvest of additional information.

In summary, I would say that a meaningful inorganic course is one in which the above philosophy of inorganic chemistry is emphasized. It does not make much difference which particular elements are used for illustration. The student must recognize the process of examining experimental data and looking for relationships which can be related to some chemical model; that is, use an inductive process in going from experimental data to a model or theory to correlate them and then reversing the process through a deductive procedure, whereby one predicts behavior in interpolated regions or perhaps even into extrapolated regions. Once the student has learned how to go through the processes of inductive and deductive reasoning from experiment to theory and back to chemical data again, he will be able to apply this procedure to both equilibrium and kinetic data. In his advanced courses he will, of course, want to become familiar with the wide range of models and adaptation of models that other people have used so that he may recognize the factors that must be considered in understanding variational trends in experimental data. Thus, in brief, a meaningful inorganic course should be based upon a framework of physical chemical theory which can be used to correlate available data, interpolate between them, and to some extent even extrapolate beyond the actually observed range.

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The Role of Kinetics in Teaching Inorganic Chemistry

The recommendation that is made in this paper for treating rate phenomena as an integral part of the course work in descriptive inorganic chemistry should be considered in the context of the philosophy of the entire course. I shall outline the philosophy which has governed the selection of the material for one of the courses in inorganic chemistry at the University of Chicago, a course which I consider salutory not only for the persons entering inorganic chemistry but for those inclined to the other branches as well. This philosophy takes for granted that descriptive inorganic chemistry is an essential ingredient in the curriculum for a bachelor's degree in chemistry; if this attitude seems arbitrary perhaps it will appear less so as the theme of this paper is developed. It also recognizes that the pressures exerted in the curriculum for general courses and the necessity of meeting the major requirements recommended by the ACS Committee on Professional Training leave little time for the study of inorganic chemistry.

If these pressures permit the student to devote only one quarter or one semester to work in inorganic chemistry, how can the time be used to his best advantage? It has seemed to me that for the purposes of training the whole chemist without demanding a complete reorganization of the subject matter of undergraduate training, this time is put to best use in the senior year after the student has developed some feeling by the study of organic chemistry for properties and reactivity in relation to structure and has been exposed to the principles governing equilibrium behavior by the study of physical chemistry. With this preparation it is possible to give an intensive, reasonably quantitative description in a selected area of inorganic chemistry which serves to generalize and illuminate the subject matter of organic chemistry and provides scope for the exercise of physico-chemical principles. With this approach, involving the application of principles to a body of information, their application becomes a habit of ordinary thought and thus enormously enhances their utility. The student is brought to the frontier of knowledge, at least in a particular area of chemistry, and gains an appreciation of the unsolved problems, theoretical and experimental, which confront the chemist. Critical discussion is possible, theories can be appraised and their deficiencies noted; and gaps in knowledge and understanding are exposed. A course of this kind is better suited to quickening the interest of the creative student than is the alternative one devoted to a survey of a wide field of information. In the limited time we are allowed, a rapid survey cannot help but be superficial. The astute student realizes that almost all the information thus acquired is forgotten soon after the final examination and can be forgiven for questioning whether the best use has been made of his time. At the advanced level the teacher is not needed to siphon information from book to notebook, but he is still useful in helping the student to form attitudes and points of view which are fundamental to a successful application of his knowledge.

In the limited time available only a limited area of chemistry can be covered with intensive, critical discussion. As far as I can see, this area can be selected arbitrarily, but some principles can be taken as governing the choice. Thus a choice made just on the basis of developing a single aspect of chemical behavior should be avoided and, therefore, a selection with respect to some area of the periodic table is recommended. Furthermore, to provide the best opportunity for inspired teaching, an area of chemistry in which the teacher is interested and with which he is especially familiar should be included. In the course at Chicago, I have chosen to discuss the chemistry of non-metals, but I find that I cannot do justice even to three groups of elements in a one-quarter course.

The three major themes that run through the fabric of the subject are: (a) What reactions are possible and how far do they proceed? (b) How do they take

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place and how fast? (c) How are the substances, their properties, and transformations understood in terms of what is known about atomic and molecular structure?

To what extent are these themes being developed in courses in inorganic chemistry? The most convenient way to assess the situation is to examine standard textbooks of inorganic chemistry. It is at once obvious that at least in modern textbooks there is considerable concern about molecular and electronic structure. Linus Pauling has had a powerful influence, particularly in this country, in the development of interest in this theme as it pertains to inorganic chemistry. The systematic application of equilibrium behavior as a useful means of describing one aspect of chemical change has been accepted less rapidly, but the indications are that it is now fairly generally used. For example the recent book by Moeller (*1*) makes consistent and excellent use of equilibrium data in systematizing inorganic reactions. The acceptance that systematic application of equilibrium principles has gained can be credited largely to the Berkeley school of inorganic chemistry and, as a product of that school, to the books by Latimer and Hildebrand (*2*) and by Latimer (*3*). There is reason to believe that kinetic behavior will begin to penetrate the teaching of inorganic chemistry also. Thus Gould enlivens the subject of his book, "Inorganic Reactions and Structure," (*4*) with a discussion of inorganic mechanisms as an integral part of the material, and a recent book by Basolo and Pearson (*5*) is devoted entirely to the subject. Advanced in this respect as these books are, they are by no means the pioneer effort. Thus Yost and Russell's "Systematic Inorganic Chemistry" (*6*) incorporates kinetics into descriptive inorganic chemistry. This book, in fact, comes closest to serving as a suitable text for the kind of course in inorganic chemistry which I am discussing; its chief deficiency is its limited coverage.

Why Kinetic Behavior?

It is proper to inquire why kinetic behavior should be considered as part of descriptive inorganic chemistry. The reasons given are basic and obvious; yet there has been such reluctance to discuss this aspect of behavior and many eminent chemists appear so willing to disqualify themselves as being sufficiently expert, that it is not out of place to state some of the obvious truths. Much of chemistry is based on meta-stability—complete equilibrium with respect to all changes takes from chemistry an essential feature, that of the possibility of a net change. Exploitation of chemical reactions, which involves controlled release of energy, involves questions of rate and mechanism. The success of preparative procedures usually depends on a favorable relation between the rates of competing reactions. The success of most measurements of equilibrium properties also depends on a favorable relation of some reaction rates. To cite an example: the value of E^0 for the Ce(IV)-Ce^{+++} half reaction would be difficult to determine if the reaction of Ce(IV) with H_2O reached equilibrium rapidly.

Rather than limiting myself to an emphasis of the importance of the subject, I would like to stress a more active feature, which is that discussion of rate behavior greatly enlivens descriptive chemistry. For example in dealing with the chemistry of $S_2O_8^{-2}$, the subjects of its structure and stability are soon exhausted. But there is a wealth of interesting information on its reactivity and the mechanisms of its reactions, or at least a wealth of interesting questions which can be asked and considered. How rapid is its hydrolysis and how is it affected by acidity? How rapid is the decomposition and how does it take place? Does it react with a particular reducing agent by a $1e^-$ process or by a $2e^-$ process? Is oxygen transferred when it oxidizes H_2O or other substances? Why is it so inert to oxidation as compared to H_2O_2? What is the mechanism of catalysis of its reactions by Ag^+? What are the properties of the intermediates derived from it in its reactions? The answers to questions such as these make up the understanding of the chemistry of the substance. The question of "how" is one of the earliest that a student asks when he first is introduced to chemical change. Some satisfaction on this point is owed to him as part of his undergraduate training.

Why is so little done with the kinetic aspect of chemical behavior in descriptive chemistry? One reason, of course, is that because little has been done little is being done. Many competent teachers of inorganic chemistry have inadequate appreciation of this part of their subject and tend to emphasize the structural and preparative aspects. Perhaps the principal reason why kinetic lore has been neglected is that it is under suspicion, in part because the subject is regarded as too complex and in part because it is felt that the quality of the conclusions made in this field is lower than in other fields. The complexity of the subject must be admitted, but this should serve as a challenge rather than a reason for avoiding it. The complexity is only somewhat greater than that of equilibrium behavior. It is greater because for every net change a variety of paths exist. But these are usually sorted out with respect to accessibility in the same way that the different chemical combinations possible for a set of reactants are ordinarily fairly widely separated in energy. Over a wide range of experimental conditions a few paths usually predominate. The subject develops by progression, from the major paths which are the easier to identify to the minor ones which may nevertheless be important in their implications. Other substances added to the system may provide new paths, but the interactions of such substances with reactants and products must equally be considered in accounting for equilibrium behavior. As to the quality of the conclusions in this field, it can be asserted that rate phenomena are no less susceptible to scientific treatment than are other aspects of chemical behavior. Theories for reaction mechanisms have been proposed which satisfy all known observations and are adaptable to new observations, and they have proved to be as serviceable as other scientific theories of similar scope. The observations of Bodenstein and his students on the kinetics of gas reactions still stand, as do the principal features of many of his proposals about mechanism. They may have been elaborated on in later work but they have not been fundamentally altered. A similar description applies to much other work which is carefully done and discussed in a conservative and critical manner. Many careless contributions have been admitted to the literature, and harm has been done by

this and by non-critical oversimplifications of the subject. The topic has been especially inviting to persons with unbridled imagination and boldness; these qualities are not without value in the field, but they are better put to use in conceiving and performing the experiments than in preparing the work for publication.

Principles of Kinetics

In the remainder of this paper I want to mention some of the principles of kinetics that are important to an appreciation of descriptive rate behavior of the kind that I attempt in advanced inorganic chemistry. These principles are developed early in the course, their discussion following immediately after the review of equilibrium principles as part of the introduction to the course, for both kinetic and equilibrium principles are regarded as essential tools in descriptive inorganic chemistry. Little development of the principles is attempted in this paper, and with one exception they will simply be mentioned and then commented on briefly.

Of concern for our purposes are the influences which temperature, pressure, concentration (of reactants, products, and other substances), and nature of the environment exert on the rate of reaction. The variations of rate with temperature and with properties of the environment are dealt with by presenting the Arrhenius, the Brønsted, and the Eyring formations, discussing briefly the significance of the various factors in the equations. In practice, little specific use is made of activation energies in arriving at ideas about mechanism, and such applications as are made do not require a refined theory. Entropies of activation may be somewhat more useful because entropies can often be fairly well estimated for various assumed structures of the activated complexes. In connection with the variation of rate with environment, the special case (and perhaps the only one that is moderately well understood) of the variation of rate with ionic strength is worth outlining. These remarks should not be taken as disparagement of the "physico-chemical" aspects of rate behavior, which are indeed problems of the most fundamental importance. But in descriptive chemistry, emphasis should be placed on those features which contribute most to arriving at conclusions about mechanisms. It is easy to confuse and discourage a student by making too detailed an analysis of features which are really not exploited later in the course.

Of the factors that affect the rate of reaction, the effect of concentration as expressed by the rate law has the greatest significance in deciding questions about mechanism, and this is the topic that is stressed most in the introductory lectures. The object of this discussion is to understand what a rate law is, what it implies about mechanism, and, just as important, to appreciate the limitations on the information it yields. Some of the ideas that I have found it worth while to develop in this connection are outlined in the following.

The Rate Law. It is necessary to stress that the rate law is an observed law and that it is not predicted from the equation for the net change; furthermore, it must be emphasized that for many systems the variation of rate with concentration is really *observed* to be a simple function of the concentration of the substances present. The rate law is valid only for the range of conditions for which it has been tested; extreme variation of the concentration may require modification of the rate law, but in a properly derived law, the modified form is more general and includes the original as a more special case.

Parallel Paths. For any net change a number of independent reaction paths exist which are revealed as additive terms in the rate law. All paths contribute simultaneously, but the relative contributions will depend on concentrations (and other conditions).

At equilibrium, for each path the forward and reverse rates are equal—the equilibrium condition is not merely that the total rate forward is equal to the total rate reverse, but it requires detailed balancing by each path. This condition is used to "derive" the form of the rate law for the reverse reaction by any path by bringing into context the rate law for the forward reaction by the same path and the expression for the equilibrium quotient. It must be appreciated that such a "derivation" is not rigorous. Obviously any power of the equilibrium quotient is an equally satisfactory means of expressing the equilibrium situation so that a rate law for the reverse reaction can be "derived" combining any of these quotients with the rate law for the forward reaction. Any success in "deriving" rate laws for reverse reactions depends on kinetic considerations: the least complex rate law is the one which is most likely to be observed.

The Activated Complex. Let us assume that we are interested in a term in the rate law for the reaction $A + B = C + D$ which has the form: $k(A)(B)$. This rate law can be interpreted in the most general way by taking it to mean that for reaction to occur some critical event in A which takes place with a probability proportional to the concentration of A must take place *simultaneously* with some critical event in B, the probability of which is likewise proportional to its concentration. This combination of critical events is called the activated complex, and it is evident that looked at in this general way the concept does not even imply close contact of A and B. (In some systems, in fact, it is a problem of current interest to learn whether A and B need be in molecular contact for reaction to occur.)

The distinction between an intermediate and an activated complex needs to be made. An activated complex is always in the act of decomposing to reactants or products, and this is the only kind of reaction which it can undergo. An intermediate on the other hand needs further activation for reaction, can in principle undergo a variety of reactions, and is in principle isolatable. There may be an intermediate which has the composition of the activated complex and almost its geometry, but because it is an intermediate some distortion of bonds is necessary to make it into the activated complex.

Kinetically Equivalent Forms of the Rate Law. This point will be developed and illustrated with a specific reaction, namely that between oxalate and chlorine in water. A term in the rate law (7) for the reaction is:

$$\frac{k(Cl_2)(H_2C_2O_4)}{(H^+)^2(Cl^-)}$$

(The concentrations referred to are the actual concentrations of the species in question, not total stoichio-

metric concentrations.) It is important for the student to realize that there are many forms of the rate law which are kinetically indistinguishable from that given. Among these forms are the following:

$$\frac{k'(Cl_2)(HC_2O_4^-)}{(H^+)(Cl^-)}; \quad \frac{k''(Cl_2)(C_2O_4^{-2})}{(Cl^-)}$$

$$k'''(HOCl)(HC_2O_4^-); \quad k''''(OCl^-)(H_2C_2O_4)$$

One form is neither more nor less correct than any other (although that form is to be preferred as a representation of the observations which expresses the rate in terms of the predominant species), and much useless argument is saved when this is appreciated. These forms of the rate law are freely interconvertible because the equilibria

$$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$$
$$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{-2}$$
$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$
$$HOCl \rightleftharpoons H^+ + OCl^-$$

are all established rapidly compared to the redox process. This being so, there is no point in arguing from kinetic evidence about whether the reaction is between $HOCl + HC_2O_4^-$ for example or whether between OCl^- and $H_2C_2O_4$.

In this connection the point should be stressed—that the rate law is undefined with respect to solvent molecules (or in fact with respect to any substance the concentrations of which have not been changed in determining the rate law). Thus, solvent molecules can always be added to the rate law without violating the kinetic observations, and if a labile equilibrium exists which eliminates solvent from the reactants, the order with respect to solvent molecules can be reduced.

Mechanisms to Rate Laws. This subject presents no particular difficulty, at least when the discussion is limited to some basic, simple cases. Among the two types of mechanisms which should be discussed are: (a) those in which there is a single rate determining step but the complication is allowed that rapid equilibria may precede it (this kind of situation is illustrated by the example in the previous section; the origin of the negative powers in the concentrations of some of the substances should be referred to); and (b) those in which there is more than one rate determining step, but the steady state approximation is applicable. The quality of the steady state approximation must be appreciated. It is that at the "steady state" the net rate at which the intermediate in question changes concentration is small compared to the rate at which the reactants change to products. This situation will always be achieved when an intermediate remains at a small concentration relative to the reactants. The steady state approximation does not require that the concentration of the intermediate remain constant—in the usual case, even for the situation in which the approximation is valid, the intermediate must change concentration by a large factor during the reaction. Three cases to which the steady state approximation is applicable and which present some basic recurring features are the following:

(a) Simple, non-catalytic intermediate:

$$\begin{array}{ll} \text{Net change:} & RX + Y \rightarrow RY + X \\ \text{Mechanism:} & RX \rightleftharpoons R + X \\ & R + Y \rightarrow RY \end{array}$$

R is the intermediate which remains at low concentrations and all steps are rate determining.

(b) Catalysis by an intermediate generated in the intrinsic reaction, i.e., chain reaction:

$$\begin{array}{ll} \text{Net change:} & H_2 + Y_2 \rightarrow 2HY \\ \text{Mechanism:} & Y_2 \rightarrow 2Y \\ & Y + H_2 \rightarrow HY + H \\ & H + Y_2 \rightarrow HY + Y \\ & H + H \rightarrow H_2 \end{array}$$

(c) Catalysis by an added substance:

$$\begin{array}{ll} \text{Net change:} & A + B \rightarrow C + D \\ \text{Mechanism:} & A + O \rightarrow C + R \\ & B + R \rightarrow D + O \end{array}$$

In each case it is important to relate the observed rate law to the mechanism and to appreciate what features are introduced into the rate law by features of the mechanism. It is also important to consider the limiting cases of the rate laws which arise when the relative values of the specific rates change. These exercises are important so that the student can develop some feeling about features of mechanisms implied by commonly observed forms of rate laws.

Rate Law to Mechanism

By far the most difficult part of the subject for the student is that of deducing a reasonable mechanism consistent with a set of facts. The reason for the difficulty is simply the student's lack of experience in chemistry. The formulation of a reasonable mechanism consistent with a rate law and certain other explicit observations invariably draws upon other chemical experience and involves many implicit chemical judgments. These judgments are made so automatically by a person of experience that it is difficult for him to see the problem from the point of view of the student, for whom a nuclear transformation is very often the only exclusion.

It is no easier to teach sophistication in this matter than in any other. But it is possible to initiate the student by helping him to develop an appreciation for precisely what the rate law implies.

Unfortunately this subject, important as it is, has not been thoroughly explored in the published literature,[1] or if it has, the conclusions are not common knowledge among workers in this field. When there is a single rate determining step, the form of the rate law defines the composition of the activated complex (except for the species of undefined order). In such systems the rate law can be used to establish the composition of the activated complex in the same way that the mass law can be applied to establishing the formula of some species which is at equilibrium with the reactants. With this in mind, the discussion of kinetically equivalent forms of the rate law can be rephrased: the rate laws are all equivalent because all define an activated complex of residual composition $(ClC_2O_4)^-$ (this formulation assumes that the Cl^+—O bond is labile). Once this is understood the subject takes on greater simplicity. Certain elements of the composition thus being defined, the important questions become: what groups not revealed by the kinetic evidence are also present? What is the arrangement of the atoms in the activated

[1] It will however be treated in a book by E. L. King, *Reactions in Solution: Equilibrium and Kinetics*, to be published.

complex? Which are the sensitive bonds? For answers to these questions, other evidence besides rate law evidence must be introduced.

A difficulty in the subject under present discussion is this: does the rate law observed imply the composition of an activated complex or is another interpretation necessary? The case in which there is a single rate determining step, and, at most, rapidly established equilibria preceding it complicating the situation, has been discussed. But many kinetic situations are not nearly so simple as this, particularly those in which an intermediate at a steady state (rather than in an amount at equilibrium with reactants) is kinetically significant. In a steady state treatment, a rate equality is written in which stoichiometry need not be preserved. The resulting rate equations, although inviting the simple interpretation given above, do not have this meaning at all. The transition from one situation to the other is often quite subtle, as can be illustrated by the following hypothetical mechanisms. Let us assume that the reaction of Cl_2 and H_2 proceeds by

$$\begin{array}{ll} Cl_2 \rightarrow 2\ Cl & k_1 \\ Cl + H_2 \rightarrow HCl + Cl & k_2 \\ H + Cl_2 \rightarrow HCl + Cl & k_3 \\ 2Cl \rightarrow Cl_2 & k_4 \end{array}$$

Then at the steady state the rate of reaction is given by

$$k_2\sqrt{k_1/k_4}\sqrt{Cl_2}(H_2) \qquad (I)$$

Let us assume now that the chain breaking step is (5) rather than (4),

$$H + H \rightarrow H_2 \qquad k_5$$

Then at the steady state the rate law becomes

$$k_1(Cl_2) + \sqrt{k_1/k_5}\, k_3\, (Cl_2)^{3/2} \qquad (II)$$

Now the rate law (I) is one of the proper kind, having some relation to the composition of the activated complex for the reaction. Examining the rate law we conclude that the activated complex consists of $^1/_2Cl_2$ (or Cl) and H_2. (Since steps 2 and 3 do not alter the concentration of Cl, Cl is at equilibrium with respect to Cl_2 and the rate is determined by the success of the attack on H_2 by the equilibrium amount of Cl.) The modification of mechanism in rate law (II) seems almost trivial. However, the mechanism is now of an entirely different kind. Neither H nor Cl are present at the equilibrium concentrations, but their concentration is determined by the rate at which they are formed and then transformed, not to the species from which they arose, but to new forms. In the resulting rate law (II), the second term does not correspond to the composition of an activated complex; (the first term which gives the rate at which HCl is formed by the process

$$\begin{array}{l} Cl_2 \rightarrow 2Cl \text{ (slow)} \\ 2[Cl + H_2 \rightarrow HCl + H] \\ 2H \rightarrow H_2 \\ \text{net: } Cl_2 + H_2 \rightarrow 2HCl \end{array}$$

with the first step rate-determining does give the composition of the activated complex for this path).

The difficult question is: how can one tell when a rate law is of the proper kind? In some cases this is quite easy. If for example we are confronted by a law such as

$$k\,\frac{(H_2)(\sqrt{Cl_2})}{(O_2)}$$

we can feel certain that the rate law cannot mean that we are making an activated complex from one H_2, one Cl, and minus one O_2. But a law such as $\sqrt{Cl_2}(Cl)$ is not absurd when interpreted as an activated complex. I am unable to formulate a satisfactory general answer for the question posed but can point out that experimental tests can be applied to distinguish the case of a single activated complex from those in which intermediates in non-equilibrium amounts are rate-determining. For the former case, the rate (keeping T, P, and properties of the environment constant) can be changed only by changing the concentrations of the reactants. Since the activated complex is at equilibrium with respect to the reactants, such reactions cannot be inhibited. When the concentrations of kinetically significant intermediates are sustained by steady state conditions, inhibition, short of consuming reactants, is possible.

This discussion has been included not because it is profitable at the beginning of the course to follow through these arguments but because the teacher should appreciate the quality of the lore in the field in order to make a critical evaluation of kinetic conclusions. The rates of many of the reactions occurring in water solution which have been studied are governed by rate laws of the proper kind, and the question of the composition of the activated complex in relation to the rate law can be raised with little danger. There is always a question as to the coverage which each aspect should receive in the introduction. My own feeling is that the best approach is to limit the introduction to a few basic principles and embellish the subject as the chemistry encountered demands it. For example, discussion of special methods such as isotopic ones can be left until they are met in practice.

Finally I should like to mention that it is important in this subject to maintain a critical, conservative attitude in reaching conclusions. Perhaps the greatest danger which confronts the person who is overconfident of his conclusions is not that he may be proved to be wrong but that this attitude may blind him to the facts. Nature continues to display more imagination than any observer.

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Inorganic Chemistry and the First-Year Graduate Student

Prior to registration, each new graduate student at the University of North Carolina is required to take four proficiency examinations covering the fields of analytical, organic, physical, and inorganic chemistry. (A student who has never studied physical chemistry may elect to postpone the examination in physical chemistry.) The examinations serve two main purposes. First, they offer a guide to the departmental advisers in registering new students for courses. Secondly, they enable the faculty to assure itself that each student, regardless of his major interest, attains a minimum comprehension of the four main branches of chemistry.

Over a period of years, it has become apparent to the author that performances of first-year graduate students on these examinations are indices of what is taught to aspirants for the baccalaureate with a major in chemistry. (Some will prefer the statement: "what is retained by the students.") Some years ago our graduate students came largely from the small colleges in the Southeast. In recent years, the graduate student body has become somewhat more cosmopolitan. Backgrounds among the current graduate student body include undergraduate or master's degrees from Wesleyan, U.C.L.A., Cornell, Amherst, New Hampshire, Penn State, College of the Pacific, Washington State, Wooster, George Washington, Bucknell, Coe, New York University, and Pittsburgh, in addition to the colleges and universities of the southeastern region. Consequently, the conclusions which will be drawn herein are not necessarily limited to one region of the country.

Each student receives a grade of pass or fail on each examination. A grade of pass means that the divisional faculty feels that the student has demonstrated satisfactory knowledge of the particular division of chemistry *at the undergraduate level.* A grade of fail means that the divisional faculty is convinced that the student should undertake remedial study (formal or informal) in the division *at the undergraduate level.* The over-all results of proficiency examinations given during the period 1953–57, inclusive, are summarized in Table 1. It must be emphasized that grades of students taking the examinations for the second time are not included.

Clearly either the inorganic background of our first-year graduate students is inadequate relative to that in at least two of the other fields, or the inorganic examinations are too rigorous. Since both students and faculty continue to tolerate the inorganic divisional examinations, I prefer to eliminate the second possibility. In fact, almost to a man, the graduate students express satisfaction with the examination.

Table 1. Results of Proficiency Examinations, 1953–57

	Analytical	Organic	Physical	Inorganic
Total students	107	106	94	106
Number passing	58	43	21	18
Number failing	49	63	73	88

At this point, some description of the pitfall which catches 83% of our entering graduate students is in order. There follow the results of some typical questions, selected from individual examinations.

Write a balanced equation to show what happens when Na_2O_2 is added to a basic solution of sodium chromite. Nineteen out of 25 students were unable to do as asked. Formulas presented for sodium chromite include $Na_2Cr_2O_3$, Na_2CrO_2, and Na_2CrO_3. I do not believe that the report by Scholder and co-workers of the synthesis of barium orthochromate(IV) is the reason for such a group of individuals considering that chromite consists of a chromium-containing oxyanion in which the chromium exhibits an oxidation state of +4! The principal product of the reaction in question was given the formula Na_3CrO_4, $NaCrO_3$, $NaCrO_4$, $Na_2Cr_2O_7$, and $Na_2Cr_2O_4$. Four students gave Na_2O as a by-product of the reaction.

Eleven out of 23 chose tantalum as more abundant in the earth's crust than hafnium, which I take to mean that all 23 were guessing.

A formula was requested for the substance, hexamminechromium(III) perchlorate. Among the answers were the following: $Cr(NH_3)_6(ClO_3)_3$, $Cr(NH_3)_6ClO_4$, $Cr(NH_3)_6(ClO_4)_3$, $Cr(NH_2)_6ClO_4$, and $Cr(NH_2)_6(ClO_4)_2$.

Fifteen out of twenty-six did not know what happens when $AlCl_3 \cdot 6H_2O$ is heated to 500°C; eleven individuals stipulated that this is a way to make anhydrous aluminum chloride.

Only 15 out of 26 knew what happens when excess aqueous ammonia is added to a dilute solution of $NiCl_2$. Four stated that no reaction takes place. Some precipitated the hydroxide, others the anhydrous oxide.

A choice was offered between the questions: (a) explain why CCl_4 is stable toward reaction with H_2O at room temperature, whereas $SiCl_4$ reacts with water violently; (b) $CrCl_3$ sublimes near 1200°C, whereas $FeCl_3$ sublimes below 200°C. Offer an explanation.

Presented as part of a Symposium on Instruction in Inorganic Chemistry, sponsored jointly by the Division of Inorganic Chemistry and the Division of Chemical Education at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

Four out of 26 students offered what the examining committee felt was a reasonable statement of explanation.

On the positive side, 23 out of 26 knew that HgO loses oxygen more easily than do CdO and ZnO, and 75% of the group answered correctly questions related to electronic configuration.

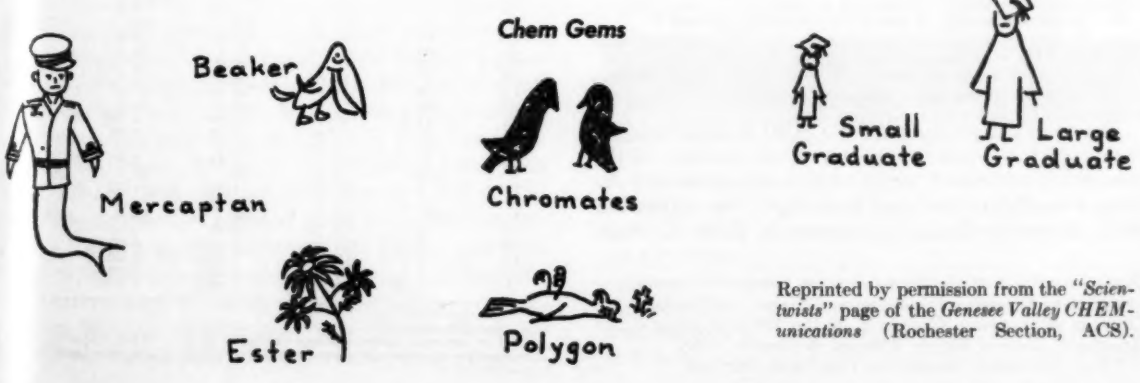
Nearly all of the students who have taken the proficiency examinations take our advanced inorganic chemistry courses. With the exception of those few who leave at the end of one semester, the same people who return such idiotic answers on the inorganic proficiency examinations prove to be intelligent young people, capable of doing graduate work. When at the end of the year they are confronted with some of the answers they wrote upon entrance, they laugh as much as I do; but it is almost universal that they have not been introduced to the *basic facts* of inorganic chemistry in undergraduate school.

The examples above have been selected with care to represent the performance of entering students year after year. As we all know, it has become passé to discuss very much descriptive chemistry during the freshman year. One such topic which has not suffered this fate is the chemistry of oxygen. It is my guess that this fact is alone responsible for 23 out of 26 students "guessing" that HgO loses oxygen more easily than CdO and ZnO. Freshman chemistry has become "theoretical chemistry." This would be an excellent state of affairs if our college freshmen had the descriptive background that is required of their English or continental contemporaries. During the second year, which is devoted by most schools to quantitative analysis, far less descriptive chemistry is being taught than in former times. I find in our own sophomore quantitative laboratory, each student learns to use an instrument which was an enigma to most of the faculty members at my alma mater fifteen short years ago. Instrumentation is the word. Perhaps it should be, but the point is that the undergraduate cannot be expected to learn the basic facts of inorganic chemistry there. The third year is devoted to organic chemistry, where the organic faculty member in charge shrewdly recognizes that a chemist needs a minimum of descriptive organic chemistry and proceeds to teach the same. In fact, I suspect that organic professors around the country are responsible for putting more descriptive inorganic chemistry into the heads of undergraduates than any other group of college professors. They tell me, by way of explanation, that it is done in self-defense. In the fourth year, a variety of things happen to American undergraduate chemists. Many take physical chemistry, which is a discipline which, if taught adequately, leaves little time for side issues. Few are the schools which require undergraduates to learn what I choose to call basic descriptive inorganic chemistry. We can hardly feign surprise at the performance of new graduate students on proficiency examinations.

We live in the era of a renaissance in inorganic chemistry. Even the least prejudiced observer must agree that great strides have been made in the discipline during the past ten years. It has become a dynamic subject, having been literally "kept alive" by a few distinguished men. If we wish to train new young men to take their place in the field, I think we owe it to them to see that the "house is built upon a rock" and not in the sand, the rock in this case being a modicum (not a compendium) of descriptive inorganic chemistry. It is fun and perhaps more important to teach theoretical inorganic chemistry, but only if our students know a few facts to begin with. In our enthusiasm over recent progress in theoretical chemistry, we neglect the the very subject matter which the theory is devised to explain.

It is my opinion that all graduate chemists should be given a reasonable foundation in inorganic chemistry. One of the most intelligent young physical chemists (a faculty member) I know came down the hall one day with a bar of sodium in his hand asking how to get "this white cover from around the sodium." It would require little effort on our part to render such a situation unlikely ten years from now. Lest I be misunderstood, let me state that I do not wish to see hordes of esoteric facts of inorganic chemistry clutter the mind of each first-year graduate student. However, I am concerned that we may have turned to the other extreme.

The author is indebted to chairman Arthur Roe, for permission to report the summary of proficiency examination results.



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The Role of the Analyst in the Preparation of High Purity Nuclear Materials

The role of the analyst in the preparation of nuclear materials of high purity was extremely important. Without his aid the processing of these materials would have been very seriously hampered if not impossible to accomplish.

The fuel used in atomic reactors is usually uranium. This uranium may be of normal isotopic composition or enriched. In order to reduce the speed of the neutrons from the fission of U^{235}, so that they may be captured by U^{238} and eventually form plutonium, it is necessary to use a moderator. The moderator used may be graphite, beryllium, or heavy water. The original work in 1942 was started with natural uranium (0.72% U^{235}) as a fuel and graphite as a moderator.

Naturally, the next question is, "What is the effect of chemical impurities in nuclear materials?" First and foremost is the absorption of neutrons. Any impurities which would absorb neutrons in the uranium itself or in the moderator would cut down the number of neutrons or might in fact stop the reaction if they were in high enough concentration. Since we must consider this problem in connection with how much the material itself absorbs, an arbitrary value known as the danger coefficient has been used.

The danger coefficient of a substance is a measure of the ability of that substance to absorb thermal neutrons compared with the ability of some reference substance to absorb thermal neutrons and is equated as follows:

$$K_s(i) = \frac{S_i}{S_s} = \frac{(N_0\sigma_i/A_i)}{(N_0\sigma_s/A_s)}$$

where:

- K_s = danger coefficient with respect to reference or standard substance
- S_i = effective area presented to neutrons by one gram of impurity (cm^2/g)
- S_s = effective area presented to neutrons by one gram of reference substance (cm^2/g)
- N_0 = number of atoms in one mole of any substance (6.03×10^{23} atoms/mole)
- A_i = atomic weight of impurity (g/mole)
- A_s = atomic weight of reference substance (g/mole)
- σ_i = atomic cross section of impurity for absorption of thermal neutrons (cm^2/atom)
- σ_s = atomic cross section of reference substance for absorption of thermal neutrons (cm^2/atom)

The total danger summation (TDS) is defined as the value which is equal to the sum of the products of the concentration of each impurity in a substance and the danger coefficient for that impurity. The values for these danger coefficients are shown in Table 1. Since we are interested in total danger summation, all impurities contribute; a large concentration of a low

Table 1. Cross Sections and Danger Coefficients for Thermal Neutrons with Respect to Various Substances

Element	Cross section[a] (10^{-24} cm^2)	Atomic weight[b]	Impurity danger coefficients[c] K(U)	K(UO_2)	K(Be)
H	0.33	1.0080	10.2	11.6	290.
Li	71.0	6.940	320.5	364.	9,220.
Be	0.01	9.013	0.03	0.04	1.0
B	755.	10.82	2,186.	2,480.	62,900.
C	0.0032	12.011	0.0083	0.0095	0.24
N	1.88	14.008	4.20	4.77	121.
O	<0.0002	16.000	<0.0004	<0.0004	<0.01
F	<0.01	19.00	<0.02	<0.02	<0.5
Na	0.505	22.991	0.688	0.781	19.80
Mg	0.063	24.32	0.081	0.092	2.33
Al	0.230	26.98	0.267	0.303	7.68
Si	0.13	28.09	0.15	0.16	4.2
P	0.19	30.975	0.19	0.22	5.5
S	0.49	32.066	0.48	0.54	13.8
Cl	31.6	35.457	27.9	31.7	803.
A	0.62	39.944	0.49	0.55	14.0
K	1.97	39.100	1.58	1.79	45.4
Ca	0.43	40.08	0.34	0.38	9.6
Sc	24.0	44.96	16.7	19.0	481.
Ti	5.6	47.90	3.7	4.2	105.
V	5.1	50.95	3.1	3.6	90.
Cr	2.9	52.01	1.7	2.0	50.
Mn	13.2	54.94	7.5	8.5	217.
Fe	2.53	55.85	1.42	1.61	40.8
Co	37.0	58.94	19.7	22.3	566.
Ni	4.6	58.71	2.5	2.8	71.
Cu	3.69	63.54	1.82	2.06	52.3
Zn	1.06	65.38	0.507	0.58	14.6
Ga	2.77	69.72	1.24	1.41	35.8
Ge	2.35	72.60	1.014	1.150	29.2
As	4.1	74.91	1.71	1.94	49.
Se	11.8	78.96	4.68	5.31	135.
Br	6.6	79.916	2.59	2.94	74.
Rb	0.7	85.48	0.26	0.29	7.
Sr	1.16	87.63	0.415	0.471	11.9
Y	1.38	88.92	0.486	0.552	14.0
Zr	0.180	91.22	0.0618	0.0701	1.78
Nb	1.1	92.91	0.37	0.42	11.
Mo	2.5	95.95	0.82	0.93	24.
Ru	2.46	101.1	0.762	0.865	21.9
Rh	150.	102.91	46.	52.	1,300.
Pd	8.0	106.4	2.35	2.67	68.
Ag	62.	107.880	18.0	20.4	520.
Cd	3,315.	112.41	923.8	1,048.1	26,580.
In	190.	114.82	51.9	58.9	1,490.
Sn	0.60	118.70	0.158	0.179	4.6
Sb	5.5	121.76	1.42	1.61	41.
Te	4.5	127.61	1.11	1.25	32.
I	6.7	126.91	1.65	1.88	48.
Cs	29.0	132.91	6.8	7.75	197.
Ba	1.17	137.36	0.267	0.303	7.7
La	8.9	138.92	2.01	2.28	58.
Ce	0.70	140.13	0.157	0.178	4.5
Pr	11.2	140.92	2.49	2.83	72.
Nd	46.	144.27	10.0	11.3	290.
Sm	8,250.	150.35	1,719.	1,950.	49,500.
Eu	4,370.	152.0	900.6	1,021.8	25,900.
Gd	39,100.	157.26	7,787.	8,835.	224,000.
Tb	44.	158.93	8.7	9.8	250.
Dy	1,100.	162.51	210.	240.	6,000.
Ho	64.	164.94	12.2	13.8	350.
Er	166.	167.27	31.1	35.3	890.
Tm	118.	168.94	21.9	24.8	630.
Yb	36.	173.04	6.5	7.4	190.
Lu	108.	174.99	19.3	21.9	560.
Hf	105.	178.50	18.4	20.9	530.
Ta	21.3	180.95	3.69	4.18	106.
W	19.2	183.86	3.27	3.71	94.1
Re	84.	186.22	14.1	16.0	406.
Os	14.7	190.2	2.42	2.75	69.7
Ir	430.	192.2	70.	80.	2,020.
Pt	8.1	195.09	1.30	1.47	37.4
Au	98.0	197.0	15.58	17.68	448.4
Hg	361.	200.61	56.4	64.0	1,622.
Tl	3.3	204.39	0.50	0.57	14.5
Pb	0.170	207.21	0.0257	0.0292	0.739
Bi	0.032	209.00	0.0048	0.0054	0.138
Th	7.0	232.05	0.95	1.07	27.2
U	7.60	238.07	1.000	1.136	28.81

[a] See Reference (*1*).
[b] See Reference (*2*).
[c] For use with concentrations expressed in %. When impurity concentrations are expressed in parts per million, danger coefficients must be multiplied by 10^{-4}.

Presented as part of the Symposium on Inorganic Chemists in the Nuclear Age before the Division of History of Chemistry and Division of Inorganic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

[1] New Brunswick Laboratory, Post Office Box 150.

cross-section element would be as bad as a low concentration of a large cross-section element.

1940–42: First Analyses of Uranium Impurities

Although the danger coefficients of the elements were not known (in the early 1940's) with the accuracy given in Table 1, enough was known to show that it was essential to analyze for all elements with a danger coefficient of about 1 or greater. As time went on other elements such as silicon, molybdenum, oxygen, and fluorine were determined for one reason or another.

Since Lyman Briggs, the Director of the National Bureau of Standards, was Chairman of the Uranium Section it was natural that the Bureau personnel were connected with the uranium project at a very early stage.

The first samples, received in January 1940, were portions of graphite electrodes. It was necessary to determine both the hydrogen in the form of water and also hydrogen which was adsorbed or combined. This was done by microchemical methods by removing the water and adsorbed hydrogen with helium, absorbing the water in magnesium perchlorate followed by burning the hydrogen to water with copper oxide and absorbing as before. The carbon was then burned to determine combined hydrogen. In March, 1940, samples of uranium powder were received to determine the absorbed water and combined hydrogen content.

Nothing more was done chemically until December 1940 when more samples of uranium were received for hydrogen analysis. At about the same time work on the separation of uranium isotopes was started at the Bureau and the microchemical laboratory of the Bureau was used in the preparation of some of the samples for use in the isotopic analyses.

In January 1941 Fermi, who had been running some neutron absorption experiments on graphite, had come to the conclusion that the major absorption of neutrons was due to boron in the graphite. Portions of his graphite were ashed and were examined spectrographically. The results obtained did not confirm his conclusions. Since it was highly important to resolve this discrepancy he asked the National Bureau of Standards if they could analyze his ash samples. A colorimetric method using curcumin was developed and the results confirmed the conclusions of Fermi. The method was finished by February 1951, and from this time on Section IV of the Chemistry Division was in business. While work continued on uranium, such as determining the hydrogen content of uranium and the density of uranium oxides which were made at the Bureau, the major effort was in determining the boron content of graphite and the materials from which it was made. The Bureau was responsible for supplying the material used by the Columbia group and early in 1941 had purchased a considerable amount of graphite from the U. S. Graphite Company. The materials used in its manufacture had been obtained and although the final graphite had a considerable quantity of boron, 2 parts per million, it was shown that the greater portion of this boron came from the foundry coke used in the process and not from the petroleum coke from which the actual rods were made. Toward the end of 1941 the Speer Carbon Company undertook the preparation of graphite using all petroleum coke with the result that the graphite made contained less than 1 part per million of boron.

In March 1941 the Bureau was asked to prepare some uranium metal. Although theoretically, this is not quite the job for an analyst, the author was asked to do this since at one time he had worked with Professor Charles James of the University of New Hampshire who had prepared massive uranium metal in 1926. The metal was made by reducing uranium tetrachloride with calcium and a melting point, determined by H. Wensel's group at the Bureau, gave about 1100°C compared to the 1850°C recorded in the literature. This was indeed startling but in the right direction. In the course of this investigation it was found that the usual calcium of commerce was very highly contaminated with boron and that, to purify it, distillation was required. About this time negotiations were in progress with Metal Hydrides Inc. to prepare powdered uranium metal. The analysis of some of their product, using a modification of the method used for graphite, showed that it was highly contaminated with boron. The major portion of this boron came from the commercial calcium used in its production. After analyzing about all known sources of calcium chloride in an attempt to find some material sufficiently free from boron to be used in the preparation of calcium by electrolysis, it was decided to install the necessary equipment at Metal Hydrides to distill the calcium of commerce. The distilled calcium proved to be essentially free of boron.

As indicated in Table 1 on danger coefficients there are a considerable number of elements with high danger coefficients. Since the purity of the original U_3O_8, obtained from the Canadian Radium and Uranium Corporation was not known, it was necessary to find out the impurities present. Early in 1940 the spectrographic section of the Bureau started work on this problem. Figure 1 shows a plate made with uranium

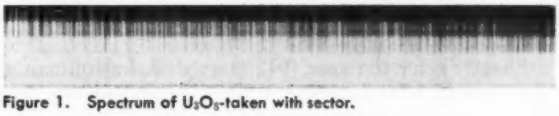

Figure 1. Spectrum of U_3O_8-taken with sector.

oxide alone. As can be seen this is a very complex spectrum, and in the initial work much time was spent in trying to unravel it to find the impurities. In spite of this handicap some progress was made. During 1941 Scribner and Mullin (*3*) developed a method using gallium oxide in a carrier-distillation technique which allowed many impurities to volatilize into the arc before the uranium. The spectrum made with this technique is shown in Figure 2. As can be seen it is

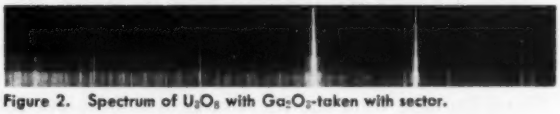

Figure 2. Spectrum of U_3O_8 with Ga_2O_3-taken with sector.

considerably simplified. This procedure, which was originally used for the determination of boron alone, was one of the most outstanding developments of the entire project.

During the same period, i.e., to the end of 1941, samples of U_3O_8 from Canada were received for chemical analysis and also the first samples of beryllium oxide and beryllium metal were received from the Chicago

group. The U_3O_8 from Canada had too much boron, rare earths, and other impurities in it and considerable work was done on leaching tests to remove the boron and the rare earths. Uranyl nitrate was also made and recrystallized and the product from this treatment was found to be considerably lower in boron and the rare earths. Since no methods for the complete analysis of uranium compounds were available, procedures in which groups of elements were determined were used: hydrogen sulfide group elements, those totally insoluble in nitric acid, and those precipitated by ammonium carbonate and by oxalic acid. Chloride, sulfate, and nitrogen were also determined.

Toward the end of 1941 N. H. Furman and his group at Princeton started work on the analysis of uranium metal from Westinghouse. The liaison between this group and that of the Bureau was excellent and a joint effort was started on the determination of impurities in uranium and its compounds. At the end of 1941 methods had been developed for boron, carbon, hydrogen, and nitrogen in uranium metal although little work had been done on other impurities.

1942: The Big Year

The year 1942 was no doubt the most important one in the whole project insofar as the chemistry of pure materials was concerned. Looking at this year in retrospect it is hard to realize that so much was accomplished in this one year.

At the start of 1942 in addition to the small scale operation at the National Bureau of Standards some uranium had been prepared by Westinghouse as well as a small amount of powdered metal from Metal Hydrides. Due to the U_3O_8 used, the material was far from satisfactory as far as impurities were concerned; the boron and the rare earths were too high. The problem of pure calcium had essentially been solved by distillation, and the major sources of impurities in graphite had been isolated.

Shortly after the year 1942 started, J. I. Hoffman of the Bureau had shown that when uranyl nitrate was extracted with ether essentially all undesirable impurities were removed. Using this procedure he and K. D. Fleischer (*4*) developed a method of concentrating the rare earths. The concentrate could then be weighed as total rare earths or examined spectrographically for individual rare earth impurities. N. H. Furman and his group using the polarograph had developed methods for cobalt, cadmium, and other elements by electrolyzing into mercury and then distilling the excess mercury.

G. N. Harrison and Rockwell Kent III of the Massachusetts Institute of Technology started spectrographic work in connection with Metal Hydride's uranium project, and H. A. Potratz went to Beverly, Massachusetts, from the Metallurgical Laboratory for the chemical work at Metal Hydrides. The Bureau obtained one of the first Baird grating spectrographs early in 1942 and was able to extend the carrier-distillation technique to many other elements. George Boyd and co-workers (*5*) of the Metallurgical Laboratory at Chicago finished the job started at the Bureau on the analysis of graphite and developed complete methods of analysis for this material.

In May 1942 F. H. Spedding, of the Chicago group, started tests using tagged rare earth ions to follow the separation of these elements from uranium in the ether extraction method. This type of procedure was used many times in the years following.

A specification committee, consisting of F. H. Spedding and L. Szilard of Chicago, C. J. Rodden of the Bureau of Standards, and R. Rosen of the Standard Oil Development Company met in May, 1942, and drew up methods of analysis of uranium trioxide, uranium dioxide, uranyl nitrate, U_3O_8, calcium hydride, distilled calcium, uranium metal, and uranium tetrafluoride.

By the end of 1942 the Mallinckrodt Chemical Works had their ether extraction operation in full swing. F. H. Spedding at Ames had made uranium metal from fluoride with calcium and some work had been done using magnesium as a reductant. Westinghouse and Metal Hydrides were making acceptable metal.

During this period chemical methods were developed among them being methods for molybdenum, titanium, manganese, and iron in uranium and manganese and boron in magnesium. The carrier-distillation spectrographic method (*3*) was extended to cover many more elements.

The question of uranium ore material became important during this year and methods were found for radium and uranium. L. F. Curtiss of the Bureau was able to determine radium by the radon method on material prepared by the chemistry department. In November, 1942, a compilation of methods was received from England (*6*). The procedure for uranium described in their report was found to be applicable to most of the ores and concentrates analyzed from that time on. While the British report gave useable procedures for many elements in uranium metal, uranium oxides, uranium tetrafluoride, and uranyl salts, several were not applicable to our materials since the limit of impurities in our materials was much lower than could be determined by these methods.

During the later part of 1942 the work on the Project was taken over by the Manhattan District of the Corps of Engineers of the Army.

During the same period the Physics Group at Chicago developed a method for testing material. This method which later became known as the "shotgun procedure" (*7*) was used to examine material to see if it was satisfactory for use. While this method did not identify impurities, it served a very useful purpose and was used by the Mallinckrodt Chemical Works for years in their production work. The essentials of this procedure are as follows: a large sample (22 pounds) of uranium oxide or metal was converted to nitrate and extracted with ether. The aqueous solution was boiled down and again extracted. This procedure was repeated until the impurities (75% or better) were concentrated in about 10 grams of U_3O_8. A beam of neutrons was sent through this U_3O_8, pressed into a pellet, and the per cent of neutrons absorbed by the impurities was measured. This was compared to samples of U_3O_8 containing known amounts of boron. In the case where high neutron absorbances were indicated it was necessary to analyze the pellet chemically to determine individual impurities.

1943: Central Control Laboratory

During 1943 the following contractors were supplying materials for the preparation of uranium metal: Eldorado Gold Mines, Limited; Vitro Manufacturing Company; Linde Air Products Company; Union Carbide and Carbon Research Laboratories; Mallinckrodt Chemical Works; E. I. du-Pont de Nemours and Company; Metal Hydrides, Incorporated; Westinghouse Electric and Manufacturing Company; Iowa State College; Harshaw Chemical Company; and Brush Laboratories Company.

Since it was very difficult to obtain or establish at the plants of the above producers adequate trained personnel and facilities to do all the work connected with quality control, a Central Control Laboratory system was established in March 1943. This Central Control Laboratory functioned for the benefit of all producers. The following groups comprised the Central Control Laboratory: Chemical Section, Metallurgical Laboratory, University of Chicago; National Bureau of Standards; Frick Chemical Laboratory, Princeton University; and Spectrographic Laboratory, Massachusetts Institute of Technology.

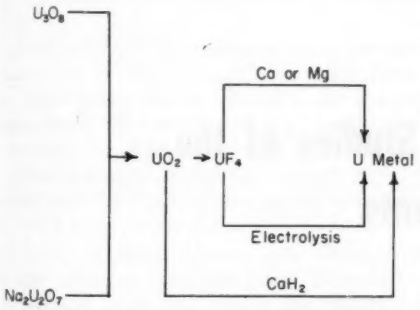

Figure 3. General flow sheet for the preparation of uranium metal.

This group, with the exception of the Metallurgical Laboratory which in August, 1943, was compelled by other work to discontinue their part in the Central Control Laboratory, acted throughout the remainder of the war. The general flow sheet for the preparation of uranium metal is shown in Figure 3.

In the above scheme the purest material was the uranium dioxide and this had to be of the required purity since no further purification was made, with the possible elimination of some boron in the uranium tetrafluoride step. Table 2 lists the analyses performed on materials at various stages of production. It will be noted that a thorough analysis on UO_2 eliminated the necessity of many analyses on UF_4. The final product, the metal, was analyzed very completely.

In addition the Central Control Laboratory had to have facilities available in order to investigate deviations from quality standards. A quote from a memo of this time reads:

> Had it not been for the availability of one of the laboratories which is to be a part of the central control group, it would have been completely impossible to carry this investigation to a successful conclusion and put the plant back into full-scale operation in a very few days.
>
> A tentative indication of possible trouble has been observed recently in another plant and an investigation is now being carried out with the cooperation of two of the laboratories in the central control group. It is hoped to eliminate the source of the impurity before the difficulty becomes acute.
>
> Such problems will arise periodically in the metal production program now planned. It is extremely important that adequate facilities be available at all times to aid in eliminating sources of contamination and keep production at the fastest possible rate.

Table 2

Analyses made on samples of UO_2

Fe; Ni; Cr; B; insoluble in HNO_3; heavy metals (Pb, Ag, etc.); assay; Mo; V; shotgun test; as complete chemical and spectrographic analyses as experience may dictate.

Analyses made on samples of feed materials

Assay; Ag; Al; As; B; Cd; Cl; Co; Fe; insolubles; Mo; Ni; Pb; rare earths; Sn; Ti; V.

Analyses made on samples of UF_4

Assay; UO_2F_2; insoluble in HNO_3; insoluble in ammonium oxalate—UO_2; Fe.

Analyses made on samples of uranium metal

B; Cl; H; Mg; As; Ag; Al; C; Ca; Co; Cu; Cr; Li; Mn; Na; Sn; Ti; Zn; Pb; Mo; V; K; Fe; Ni; N; Cd; shotgun test; rare earths; assay; density; insoluble in HCl (Oxides); insoluble in HNO_3; and such other analyses as experience may dictate.

The Central Control Laboratories also had to develop methods of analysis for certain elements for which no method, or ones of questionable reliability, were available.

As a result during 1943 methods were developed for all required elements. Since the spectrographic method had certain limitations the chemist devised methods for separating the refractory element group (*8*) such as tantalum, tungsten, etc., which could be extracted with cupferron as well as the platinum group elements (*8*) which could be concentrated using gold as a carrier. The concentrates could then be run spectrographically.

The elements analyzed spectrographically with their present (1958) limit of detection are given in Table 3.

Table 3. Present (1958) Lower Limit of Routine Spectrographic Determination of Impurities in Uranium Metal and Compounds

Element	Amount (ppm)	Element	Amount (ppm)	Element	Amount (ppm)
Carrier-distillation concentration method on oxide					
Ag	0.05	Cs	8	Na	0.5
Al	5	Cu	0.3	Ni	2
As	5	Fe	1	P	50
Au	0.3	Ge	0.5	Pb	1
B	0.1	Hg	10	Rb	1
Ba	10	In	0.5	Sb	10
Be	0.1	K	2	Si	3
Bi	0.5	Li	0.1	Sn	1
Cd	0.07	Mg	0.5	Tl	3
Co	1	Mn	1	V	5
Cr	3	Mo	2	Zn	20
Examination of refractory concentration in Bi_2O_3					
Cb	3	Pd	0.5	W	40
Ga	1	Ta	40	Zr	1
Hf	10	Ti	3	...	...
Mo	1	V	1	...	...
Examination of concentrate of rare earth oxides					
Ce	<0.1	La	<0.1	Tb	1.0
Dy	0.04	Lu	<0.5	Th	1
Er	0.04	Nd	<0.5	Tm	0.04
Eu	0.02	Pr	<0.5	Y	<0.1
Gd	0.04	Sc	<0.1	Yb	0.004
Ho	0.04	Sm	0.3	...	...
Direct examination of oxide					
Ca	2	...	...	...	...
Examination of Pt metal concentrate in Au					
Ir	100	Pt	1	Ru	5
Pd	5	Rh	20	...	...

As time went on the uranium metal was improved in quality so that at the end of the war, ton quantities of almost atomic weight purity uranium were being prepared. Also the methods of analysis were improved and modified as indicated in the "Analytical Chemistry of the Manhattan Project" (*9*) but for all intents and purposes the analyst in 1943 was able to do all the work that was required of him. Needless to say without his assistance the preparation of pure uranium would have been considerably hampered if not impossible to accomplish.

Different methods were developed in the years to follow by chemical means as well as by employing techniques used primarily by the physicist such as vacuum fusion for oxygen, X-ray fluorescence and absorption for uranium, neutron activation for impurities, and mass spectrometric measurements for U^{235} content. The analyst during this time has become a hybrid chemist-physicist.

Although the above discussion has centered on uranium, essentially the same methods were used for thorium, zirconium, beryllium, and some of the other elements used in nuclear reactors.

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Ion Exchange Studies of the Actinide Elements

A review of the actinide elements and ion exchange divides itself logically into one section considering the elements with atomic number 89 through 94, i.e., Ac, Th, Pa, U, Np, and Pu and another section covering the tripositive trans-plutonium elements. The ion exchange studies of the first group (Ac–Pu) have been discussed by Hyde (*1*) in his 1955 Geneva Conference paper and more recently by Katz and Seaborg (*2*) and will only be briefly reviewed at this time.

Unlike Pa, U, Np, and Pu, actinium and thorium do not form anionic chloride complexes to any appreciable extent. Their separation from other elements, therefore, is achieved by use of Dowex-50 cation resin exchanger. Both Ac(III) and Th(IV), because of their charge and size, will adsorb on Dowex-50 very strongly. The elution behavior of actinium as a function of hydrochloric acid concentration has been reported by Diamond, Street, and Seaborg (*3*). Like actinium, thorium elutes very slowly in either hydrochloric or nitric acid of any concentration. Both actinium and thorium may be removed from cation resin as chelate complexes by strong ammonium citrate or lactate solutions as reported by McLane and Peterson (*4*) and Asaro, Stephens, and Perlman (*5*). Adsorption of thorium on anion resin from 8 *M* nitric acid has been used by Kraus and Nelson in separations from U(VI) (*6*).

Separations involving protactinium, uranium, neptunium, and plutonium are most effective with anion exchange resins since the different complexing powers of the several oxidation states of these elements allow a wide variation in anionic complex formation. Table 1 summarizes the behavior of these elements with hydrochloric acid.

Table 1. Adsorption of Pa, U, Np, and Pu from Hydrochloric Acid on Dowex-1 Anion Exchange Resin

Oxidation state	Pa	U	Np	Pu
III	...	...	...	None
IV	...	Above 8*m*	Above 4*m*	Strong above 2.5*m*
V	Strong above 8*m*	...	Strong above 4*m*	...
VI	...	Strong adsorption above 6*m*		

For example, it can be seen that after adsorption of Np and Pu in the (VI) state from strong hydrochloric acid solution, e.g., 8 *M* HCl, reduction to Pu(III) and Np(IV) by a solution 0.1 *N* in hydroiodic acid and 8 *M* in hydrochloric acid permits the elution of plutonium. After removal of all the plutonium, the neptunium may then be eluted by use of 0.5 *M* HCl.

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Kraus, *et al*, (*7*) have separated U(IV) from U(VI) as well as Th, Pa, and U from each other, using anion resin with hydrochloric acid and hydrochloric-hydrofluoric acid mixtures. Sulfate and carbonate solutions have also been used in anion resin separations of uranium (*8*). Because of the obvious connection with reactor fuel processing, anion exchange studies of U and Pu in particular have occupied chemists at almost all the atomic energy installations both in this country and abroad. Cation resin studies with Pa, U, Np, and Pu are relatively few and not as important, with the exception of Pu(III), which has been studied with the other trivalent transplutonium elements.

In considering the ion exchange investigations performed with the transplutonium elements two facts should be kept in mind. First of all, very much is owed to rare earth ion exchange studies. Thus, Boyd, Ketelle, and co-workers, Spedding, Powell, and their co-workers, Mayer, Freiling, and Thompkins and many others are the unsung researchers of this review. Secondly, many of the actinide studies have been performed primarily to learn how to achieve faster and more complete separations. This emphasis on technique has left us in many instances with excellent separations without a good understanding of why they are excellent.

A general scheme for isolation of a particular actinide involves coprecipitation with lanthanum carrier and the rare earth fission products, an ion exchange separation from the rare earths, and finally an ion exchange separation of the individual actinides from each other. The attempts to better the latter two separations constitute the bulk of the ion exchange studies of the transplutonium elements.

Thompson, Morgan, James, and Perlman (*9*) described the elution behavior using Dowex-50 cation resin exchanger and ammonium fluosilicate. Of importance here was the fact that the lanthanides from lutetium through promethium eluted ahead of curium and americium. About the same time ammonium citrate was used by Cunningham and Thompkins (*9*) to separate curium and americium. Since promethium and americium eluted together in this system, lanthanum through neodymium eluted after americium and curium. So the fluosilicate elution eliminated the transneodymium lanthanides and the citrate, the subneodymium lanthanides, leaving americium and curium relatively pure from the lanthanides and from each other.

However, the fluosilicate elution was time consuming, and was soon replaced by an important system introduced by the studies of Street, Diamond, and Seaborg of hydrochloric acid-Dowex-50 elutions (*3*). It was found that the actinides behaved differently than the lanthanides in concentrated hydrochloric acid elution making possible the effective separation of the two elemental groups from each other. Up until approximately 6 *M* hydrochloric acid the value of the distribution coefficient between resin and solution phases was the same for both the lanthanide and tripositive actinide elements. Above 6 *M* acid, the lanthanides showed increased preference for the resin phase compared to the actinides such that the value of the ratio between the distribution coefficients of americium and promethium in concentrated hydrochloric acid approached ten. The separation of the actinides from each other was not sufficient to be useful, but the first lanthanide eluted in almost twice the volume necessary for the actinides, providing quite effective separations.

Later, use of 20% ethyl alcohol solutions saturated with hydrogen chloride much improved the group separation (*10*). The suggestion by Diamond, *et al.* (*3*) that the increase in complexing by the actinide elements in concentrated HCl may reflect the utilization of 5*f* orbitals in hybrid covalent bonds is of considerable interest.

The possibility of utilizing ammonium thiocyanate as an eluant has been studied at Berkeley (*11*). With anion exchange resin and concentrations of NH_4SCN in the molar range, no simple elution order was present. However, excellent separations from the lanthanides were achieved and Coleman and co-workers (*12*) at Los Alamos have used thiocyanate elutions in the separation of near gram amounts of americium from over 100 grams of lanthanides with considerable success. In their procedure the rare earths were eluted from Dowex-1 anion resin with 5 *M* NH_4SCN at which concentration the Am was moved only very slightly down the resin bed. Then the Am was stripped from the resin in 0.1 *N* HCl. In thiocyanate as in concentrated hydrochloric acid, the actinides demonstrate a greater complexing strength than the lanthanides.

Groups at Livermore and Berkeley (*13*) have used anion resin columns with concentrated lithium chloride solutions for similar macro scale separations with satisfactory results. However, the fast neutron flux from Li (α, n) reactions produced by the high alpha activity levels present from the actinide elements makes this less feasible than the thiocyanate system.

To separate the actinides from each other, alpha-hydroxy organic acid anions have proved the most successful as the chelate formation allows greater specificity than with inorganic anions. The early use of ammonium citrate has been mentioned. More recently glycolate, lactate, and alpha-hydroxy isobutyrate have been the eluants in use. For these monobasic anions the important equations are:

$$M^{+3} + 4X^- = MX_4^- \qquad (1)$$

$$M^{+3} + 3NH_4R = MR_3 + 3NH_4^+ \qquad (2)$$

where M^{+3} represents the actinide ion, X^- the organic anion, the R the sulfonic anionic resin site. Because of the lanthanide contraction effect, both (1), the complexing reaction, and (2), the ion exchange reaction, work to remove the actinides in inverse order of their atomic number. Since equation (2) is a function of the particular resin and the hydrated ionic radii, increased separabilities with different eluants are attributable (for the same resin) only to equation (1). The experimental setup and operating techniques are relatively simple and have been described at length in an earlier publication (*10*). Operating temperature is maintained at elevated temperatures (87°C) only in order to improve the kinetics as the separation factors seem to have very low temperature coefficients.

A table of separation factors for some eluants is shown in Table 2. Tartrate was studied by Glass (*14*), lactate by Glass (*14*) and groups at Naval Radiological Laboratory (*15*, *16*) and at Berkeley (*10*). Glycolate

Table 2. Separation Factors (Cm = 1.00)

Eluant anion	Cf	Cm	Am
Citrate	0.42	1.00	1.17
Tartrate	...	1.00	1.3
EDTA	0.18	1.00	2.04
Glycolate	0.68	1.00	1.17
Lactate	0.45	1.00	1.18
Mandelate	0.35	1.00	1.18
α-Hydroxy *n*-butyrate	0.26	1.00	1.20
α-Hydroxy iso-butyrate	0.25	1.00	1.40

was studied intensively at Argonne National Laboratory and the Naval Laboratory and was reported on by Stewart at the 1955 Geneva Conference (*17*). Fuger at Berkeley studied EDTA (*18*) while the remaining data is from Thompson, Harvey, and Choppin at Berkeley (*10*). Smith and Hoffman (*19*) at Los Alamos and Milstead and Beadle (*20*) at Harwell have obtained similar separation factors for isobutyrate at room temperature and with different resins. While EDTA gives the largest separation factors when the separations and column operating difficulties are assessed together, alpha-hydroxy isobutyrate is more favored. It should be noted in this evaluation of EDTA elutions that this is a peak elution technique and not the band elution process developed for the lanthanides by Spedding, Powell, and co-workers.

The citrate and isobutyrate elutions have provided the strongest initial chemical evidence for the first synthesis of all the actinide elements beyond curium. Using the analogy with the known separation factors of the lanthanide elements, it has been possible to predict, a priori, the elution position of yet undiscovered elements through Z = 103. Finding an activity with the predicted nuclear properties in the predicted elution position has satisfied physicist and chemist alike. Ability to make such predictions with confidence has aided greatly in planning the chemical techniques for new element experiments.

Two years ago Holm (*21*), at Berkeley on leave from the Nobel Institute of Physics, showed that the actinides could be adsorbed on anion resin from isobutyrate solutions. From analysis of data from the author's laboratory on the behavior of thulium it is possible to show that this implies the formation of the TmB_4^- anion. In Figure 1, the logarithm of a quantity proportional to the distribution coefficient has been plotted as a function of the logarithm of the isobutyrate concentration; the descending slope provides information on the charge of the complex and hence on its composition (*22*). Since curium shows the same behavior, this demonstrates a case of coordination number eight for the tripositive actinides.

Table 3. Data Obtained by Ion Exchange

Ward and Welch	
$M^{+3} + Cl^- = MCl^{+2}$	$K_1 = 14.7$ (Am, Cm, Pu)
Fuger	
$M^{+3} + Y^{-4} = MY^-$	$K = 10^{19.09}$ (Cf)
	$= 10^{18.45}$ (Cm)
	$= 10^{18.16}$ (Am)
Odenheimer and Choppin	
$Cm^{+3} + B^- = CmB^{+2}$	$K_1 = 290$
$CmB^{+2} + B^- = CmB_2$	$K_2 = 104$
$CmB_2^+ + B^- = CmB_3$	$K_3 = 11$
Gel'Man, *et al.*	
$Pu^{+3} + 2C_2O_4^{-2} = Pu(C_2O_4)_2^-$	$K = 10^{9.15}$
$Pu^{+3} + 4HC_2O_4^- = Pu(HC_2O_4)_4^-$	$K = 10^{10.96}$

Only one study has been made of the actinide-resin interaction itself (*23*); 0.1 *M* perchloric acid was used with Dowex-50 X-4. The comparison of the distribution coefficients for americium and curium with the lanthanides confirmed the opinion that the ionic radius was the major factor for ions of the same charge as the actinides adsorbed to the same extent as the lanthanides of comparable radii. Information was obtained on the free energies of formation of the metal resinates as well as on the heats and entropies of adsorption in this same study.

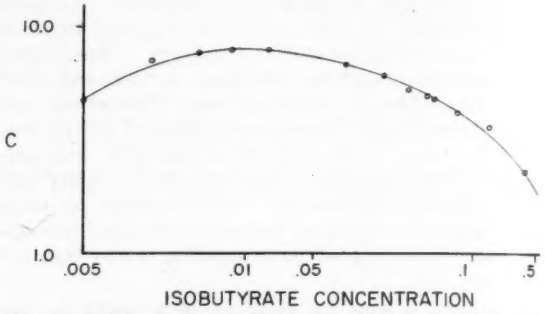

Figure 1. Number of column volumes minus one to the elution peak maximum versus isobutyrate concentration.

Finally, in attempts to better understand the physical chemistry behind the separation techniques, several groups have used ion exchange to study complexes using the equilibrium distribution technique. Some results are shown in Table 3. Ward and Welch (*24*) are English workers who studied the stability constant of the monochloride complexes of Pu, Am, and Cm. Fuger (*18*) studied the EDTA complex of Am, Cm, and Cf, finding very high stability constants. The third work was an investigation of the successive stability constants for curium with alpha-hydroxy isobutyrate (*25*), while the final data is from a Russian report of the constants of Pu(III)-oxalate complexes by this method (*26*). With only trace amounts of trans-curium actinides available at present, and with the chemical difficulties inherent in the high alpha activity levels of macro scale investigations, it would seem that ion exchange studies on the tracer level offer one of the best means of investigating actinide chemistry.

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Inorganic Chemistry in the Nuclear Age

A historical perspective

Science is now visibly among the most potent of all historical forces. Every man is affected by, and every government is concerned with, the means science gives for attaining economic abundance and for securing advantage in power politics. Visions of "one world," united and indivisible, and nightmares of a violence-destroyed planet are no longer impossible dreams. Which way man turns the creative and distinctive potential of applied science depends on his reading of history.

Science has created a second industrial revolution. The commodities and weapons this revolution will bring are second in importance to the ideas it generates and the way they inspire people. Science has already so transformed the Western World that the old Marxist criticisms of nineteenth century captialism have no valid ground upon which to grow.

Whatever their other differences, both the democratic capitalist nations and the authoritarian communist enclave agree on the emergent importance of technical concepts in human culture. As economic and government activities become increasingly technically directed, governments and citizens both can retain an effective voice in them only by understanding what events and what people are important to the advance of science and technology. Widespread education of laymen in the history of science can help this understanding.

The importance of the history of science is that it forms an easy bridge between what the layman has been taught in school and what his present duties as a citizen require.[1] The struggle of human beings to bring about a desired result has the same appeal in whatever framework it is presented. The story of past failures or of a long period of patient search or building is more understandable and memorable than a bare announcement of research success. If scientists took more interest in reporting the history of their researches and the history of their own fields of endeavor, public consciousness of who and what scientists are and of what they have done and are capable of doing would be much more advanced. Once made thoroughly public, new ideas and ways of thinking, as Guy Stanton Ford put it, "shape folkways to which laws and institutions must ultimately conform."[2] In illuminating the past, a scientist can help the future of his fellow citizens and of his colleagues.

The fate of America is tied to progress in nuclear technology. The chemistry underlying nuclear progress is essentially inorganic chemistry. Sunday supplement accounts which sound fantastic to the layman do not give him the understanding he needs as a citizen. Presenting inorganic chemistry in historical perspective would create a body of reference which science writers could use to give depth to accounts in nontechnical publications.

Inorganic Chemistry Before the Twentieth Century

Minerals, ores, and the materials made from them have qualitative differences that are more easily discernible than those found in the materials of living

Presented as part of the Symposium on Inorganic Chemists in the Nuclear Age before the Division of History of Chemistry and Division of Inorganic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

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structures. Whether they were alchemists, iatrochemists, phlogistonists, or pneumaticists, the forerunners of systematic chemistry were able to work out many relations in what was then called mineral chemistry, while plant chemistry and animal chemistry were only occasionally advanced. The application of weighing and of the measurement of gaseous volumes to the study of chemistry in the seventeenth and eighteenth centuries was most easily made to substances deemed to be chemical individuals either by qualitative distinguishment or analysis, or by chemical separation. Thus the quantitative data needed for the systematization of Lavoisier and Dalton were found in the area of "inorganic chemistry" as we known it today. Inorganic chemistry, the oldest of the chemical sciences, was the first to benefit by a systematization. This same systematization also served to put a firm rational basis under quantitative analysis, which had grown much from the study of minerals and the assay of ores and pigments. Quantitative analysis, turned to the study of natural products, began to measure differences that in time served as the basis for systematizations whose results led to newer chemistries that challenged the dominance of inorganic chemistry.

The successors of Lavoisier and Dalton, among them Avogadro, Berzelius, and Mendeleev, carried the systematization of inorganic chemistry on as far as the molecular and atomic theories that had then evolved permitted. Within the precincts of thought inspired by theories of this molecular-atomic period, only general, but not detailed studies of the properties and structures of inorganic compounds could be made. Inorganic chemistry no longer blazed its own way and the way of all chemistry with startling and significant new generalizations. Its pursuit became routinely preparative, and its literature became increasingly descriptive in nature. Whatever its applications in a growing complex of extractive processing industries were, pure inorganic chemistry, lacking new intellectual capital, descended to a level that with few exceptions was moribund. In America, where traditions of an earlier age were few and far between, inorganic chemistry became more of a museum science than it did in Europe.

This decline might have been less severe were it not for four factors. The first was the rapid rise of organic chemistry and of physical chemistry, based on the same systematization that had arisen out of the study of inorganic chemistry. The second was the difference in the way the "inorganic" and the "organic" chemistry industries were able to operate. This was based in part on the greater utility of molecular-atomic concepts in organic chemistry than in inorganic chemistry. In part it was based on the fact that the older inorganic industries were working out the first industrial revolution, while the new synthetic organic industries were initiating the second industrial revolution. The third factor that made the decline of inorganic chemistry so severe was that the few bright flashes that might have illuminated it occurred in separated areas of study whose correlation was beyond the power of molecular-atomic theory. Finally, the teaching of intellectually sterile subjects often attracts uncreative mentors who rarely inspire students to great efforts. Each of these four factors is a study in itself, and the results of each such study would be a lesson for our own times. Limited space permits only the statement that the way in which these factors interacted with each other was again more severe in America than it was in Britain and on the continent. Even today, the inorganic chemistry taught in our colleges and universities has recovered from a prolonged blight only in a few happy instances.

Inorganic Chemistry in the Twentieth Century

The renascence of inorganic chemistry in the twentieth century is one of the most impressive facts in the recent history of chemistry.[3] The revolution in physics initiated at the turn of the century ushered chemistry into an electronic-nuclear period that has far surpassed in power and fertility the molecular-atomic period of the last century.[4] While the coming of this new period has added to the intellectual capital of all of the older chemical sciences and has created some new branches of chemistry, it has completely revitalized the thinking of inorganic chemistry. A large number of factors are working together to make the renascence of inorganic chemistry one of the largest outgrowths of the century's general increase in scientific activity. Again, each of these would itself be a large study. All that can be outlined here is an undetailed general story touching on some of the many advances that have been made in modern inorganic chemistry.

The electronic theory of the atom worked out by Niels Bohr provided an immediate basis for a qualitative explanation of chemical combination on the basis of static atomic models by Kossel, Bury, Langmuir, and Lewis. At the same time Bohr's work provided a basis for refinements of a quantitative explanation of the spectroscopy of atoms on the basis of dynamic atomic models by Sommerfield, deBroglie, and Schrodinger. Hund, Mulliken, and London extended this work to a quantitative description of simple molecules. Quantitative explanations of chemical combination started to emerge as chemists trained in the mathemtics used in the new physics, like Linus Pauling, studied the nature of the chemical bond in detail.

While some studied the energies and forces involved in chemical bonding, others were applying the new concepts of quantum theory to the collisions of atoms and molecules and to the excitation of these into chemically reactive excited states. Out of this approach, and out of the quantum-mechanical statistics that were the new analogue of older statistical mechanics, more detailed techniques for studying the rates and mechanisms of chemical reactions emerged. These studies were aided tremendously by the development of tracing techniques, some based on radioelements, and others on nonradioactive isotopes. Such techniques permitted the exchange of chemically identical atoms to be studied and led to unequivocal determinations of reaction mechanisms and over-all reaction kinetics.

The discovery of radioactivity by Bequerel, its use by the Curies in following chemical separations, and the early employ of radioactivity by such chemists as Paneth and Fajans in studying the preparations and stabilities of inorganic materials and free radicals opened up a new powerful technique that became of

[3] Nyholm, R. S., J. Chem. Educ., **34**, 166 (1957).
[4] Bulloff, Jack J., J. Chem. Educ., **34**, 452 (1957).

wide utility once artificial radioisotopes could be produced. Radiochemical methods have evolved to the point of ultimate chemical accuracy, that of determining the nuclear and chemical properties of new chemical elements from samples of one or a few atoms. This advance has come from the University of California Radiation Laboratory, where Seaborg, Segre, MacMillan, and others have opened a whole new chemistry of transuranic elements by ultramicroradiochemical study.[5] Only radioactive studies could have closed the gaps in the periodic table corresponding to technetium, promethium, astatine, and francium.

The discoveries of the isotope ionium by Boltwood, the notion of isotopy put forward by Soddy, the early studies of the leads produced by different natural radiodecay series by T. W. Richards and his collaborators, uncovered a phenomenon that modified the nineteenth century notion of chemical species markedly. The contemporary work of Fedorov on minerals and of Kurnakov on synthetic materials that did not obey Dalton's laws of definite proportions also attacked these molecular-atomic notions. Such work led in time to many modern ideas of intermetallic compounds and the metallic state, and to quantum theories of semiconductors, ferroelectrics, thermoelectrics, and other solid-state materials. In studying the latter, the application of isotopes and the study of iostope effects has completed the downfall of many stoichiometric notions still honored in the textbooks.

The study of the positive rays that had been discovered by J. J. Thomson enabled Aston to determine the isotopic composition of a good many chemical elements shortly after World War I. The data gathered permitted conjectures to be made of the patterns of distribution of stable isotopes among the elements. In time the mass spectrograph became so precise that nuclidic atomic weights accurate to parts per million supplanted chemical atomic weight determinations. In Aston's time, the mass spectrograph was sufficiently accurate to detect mass defects of nuclide atoms with certainty. The data that would permit nuclear energetics to be systematized were being gathered on this as well as on the other fronts of radioactivity, radiation chemistry and physics, and nuclear reaction.

The discovery of heavy hydrogen by Urey, and the development of techniques such as those of Clusius and Dickel for separating isotopes of light elements, gave the inorganic chemist tracers at the low end of the periodic table that augmented the natural radiotracers available at the high end of the table. The early work of the Joliots on neutron irradiation uncovered the possibility of finding radiotracers for many chemical elements. The subsequent inventions of improved linear accelerators, van de Graaff generators, cyclotrons, and the higher powered accelerators of many kinds, and of nuclear reactors have made it possible to have a variety of suitable tracer isotopes for almost any chemical element.

The work on radioelements and isotopes, combined with observations made by use of accelerators and reactors, has led to a systematization of nuclear phenomena and to more precise ideas of nuclear size and nucleon regularities in nuclei. In turn, this has aided the growth of nuclear chemistry directly, and of inorganic chemistry indirectly.

Roentgen's discovery of X-rays was followed by the study of their spectra. Moseley established atomic numbers, which Goldschmidt had inferred from the scattering of electrons by thin metal foils, on a rigorous basis by means of such studies. This work led to the modern periodic table, based on atomic numbers rather than on atomic weights, and arranged to reflect the periods dictated by the adoption of Pauli's exclusion principle. In another direction, Max von Laue used crystals as diffraction gratings for X-rays, and structural chemistry had the new and powerful tool of X-ray diffraction.

Besides X-ray diffraction, electron and neutron diffraction have been added to the techniques that structural chemists can use today. The location of electrons in chemical structures, of atoms in complex ions, molecules, giant molecules, and polymers, of ions, atoms, and molecules in crystals, and of defects or strains or domains in aggregate structures has led to many important contributions to the detailed study of inorganic systems. Such observations, coupled with spectroscopic, magnetochemical, ferromagnetic, ferroelectric, thermoelectric, and other techniques uncovered in this century today give inorganic chemists the ability to answer questions that their predecessors could not even begin to frame. At the same time these answers are gradually being organized into a unified framework like that suggested by Yost and Russell.[6]

Thus in the twentieth century inorganic chemistry has used electronic-nuclear thinking to progress from qualitative to quantitative notions of valency, bond formation, bond structure, crystal structure, atomic arrangement, and a host of other microscopic properties that affect the microscopic behavior of inorganic systems. In regaining its ability to blaze its own way, inorganic chemistry can again blaze the way for progress in other sciences.

Applied Inorganic Chemistry in the Twentieth Century

The technical difference between the first and second industrial revolutions lies in the way they utilized science. In the older revolution, results long known in science were applied to engineering and industrial problems. In the present revolution, research is deliberately carried on to uncover new solutions to present and prospective problems, and such research is often aimed at uncovering basic facts. While modern inorganic chemistry has contributed extensively to the older extractive and processing industries that have graduated to this kind of research, it is in the newer industries that its contributions are best illustrated. A few of these illustrations suffice to show the new importance of inorganic chemistry in every man's endeavors.

Usually materials processing has been limited to the use of relatively low pressures and temperatures compared to those at the earth's core, in the center of stars, or in the heart of thermonuclear explosions. The General Electric Company's process for making diamonds operates at 1,500,000 psi and 2000°C. Borazon,

[5] Seaborg, G. T., et al., Symposium on "The New Elements," J. Chem. Educ., 35, 2–44 (1959).

[6] Yost, D. M., and Russell, H., Jr., "Systematic Inorganic Chemistry of the Fifth and Sixth Group Nonmetallic Elements," Prentice-Hall, Inc., New York, 1946.

boron mononitride, is isolectronic with diamond and is prepared at 975,000 psi and at about 1500°C. It should be noted that Irving Langmuir of the General Electric Laboratory was interested in isosteres, i.e., isoelectronic compounds, forty years ago.

The rare earth elements, with their interesting magnetic and alloying properties are now produced on a large scale. Until the 1930's the separation of lanthanides was accomplished by multistage fractionation. The discovery of unusual oxidation states of these elements from valence-electron considerations, and the development of ion-exchange and other techniques, notably by Spedding and his co-workers, has permitted the industrial separation of rare earth elements of high purity at a tremendously lowered cost and increased output.

The light metals represent new hope for aeronautic and astronautic designers with their eternal problem of preserving structural strength while saving every ounce of weight possible. For this, titanium has been much publicized, and the alloying of aluminum, magnesium, beryllium, and even lithium to increase their strength and chemical inertness has been widely discussed. Other little known metals may in time perform similar functions better. Scandium may be one such metal. It is possible that hydrogen and ammonium can be prepared as stable metals by high pressures. The latter was prepared as an amalgam over a century ago.

The "high energy" substances of interest as propellants offer an indirect solution to the astronauts' weight-strength problem. The availability of more energetic fuels makes it possible to work with less esoteric and more tractable structural materials and to plan for larger pay loads. Inorganic achievements that fulfill such aims include the large scale preparation of elemental fluorine, hydrazine, boron hydrides, perchloryl fluoride, and powdered metals.

"Nuclear purity" is a requirement of many materials used in nuclear technology. Boron is a thousandfold better absorber of neutrons than carbon; carbon used in nuclear reactors to slow down neutrons to the speed needed to keep the reactor producing must be exceedingly low in boron. Similarly, zirconium used in submarine reactors must be low in hafnium. Casings for clean nuclear bombs must be free of materials that become radioactive from the radiations of a nuclear explosion. Efficient nuclear fuels must be free of impurities that stop fission or thermonuclear chains. The requirements of nuclear purity have led to the pioneering development of techniques such as sequestration by ethylendiamine-tetraacetic acid, separation by liquid-liquid extraction, and separation by ion-exchange columns. These techniques are finding a place in many sections of modern industry.

The Scientist's Obligation: An Informed Public

Since the ordinary citizen may live or die according to the way science grows and is applied, he has a right to know that it is directed by people qualified to do so. He has a right to insist that the goals of research and of the application of science be appropriate to the common welfare and the national interest. These ideas should be startling only to scientists who have forgotten their own education in civics. More than two decades ago, Guy Stanton Ford said that the story of the Constitution of the United States since 1787 had been mainly that of science and technology.[2] The word "democracy" is not in the Constitution. Today's democracy was an outgrowth of industrial revolution, of mills, canals, railroads, coal, steel, oil, metals, and power. Its death on the morrow can be assured by the mismanagement of our intellectual and capital resources for research and development.

As B. D. Thomas put it,[7] the technical man has been drawn into the stream of human events by the circumstances of the last two decades in such a way that he has become the custodian of much of civilization. It thus becomes a vital professional obligation for technical men to inform not only their colleagues but also the public of the progress and meaning of their studies. This does not mean that chemists have to write press releases; but they have to report the story of their achievement as well as the achievement itself. The American Chemical News Society Service and the science writers it reaches can be relied on to relay any such report that can be made interesting to the general public. Further, inorganic chemists who can speak and write a language that laymen can appreciate need not fear that their subject will be dull. The man in the street has always appreciated straight stories and early warnings.

[7] THOMAS, B. D., *Battelle Technical Review*, **7**, No. 9, 3 (1958)

"Valence Structure" Charts Available

In response to numerous requests for the "Valence Structure of the Elements" chart appearing in THIS JOURNAL, **35**, 541 (1958) (see also *Selected Readings in General Chemistry*, Chemical Education Publishing Co., Easton, Pennsylvania, 1959, p. 92), ozalid prints $8\frac{1}{2} \times 11$ in. suitable for student notebooks may now be obtained at cost from Photo Service, State University of Iowa, Iowa City. These will be furnished postpaid at 7¢ each up to 100 copies per order and 6¢ each for 100 copies or more. Minimum order acceptable: $3.50 (50 copies).

Proceedings of the

Pacific Southwest Association of Chemistry Teachers

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Poliomyelitis Virus:
Current Knowledge of Physico-Chemical Structure

Luria has offered this definition: "Viruses are submicroscopic entities, capable of being introduced into specific living cells and reproducing inside such cells only (*1*)." Studies of the physical and chemical nature of such entities as well as their biological nature have occupied many investigators for some time. In recent years the use of tissue culture for the propagation of animal viruses has been a boon to virus research. Monkeys were necessary in early work with poliovirus, while later the virus was adapted to rodents. Currently most poliovirus studies are aided by cultures of monkey or human cells *in vitro*.

It was evident in early studies that poliovirus was among the smaller and more stable viruses. Attempts to visualize the virus particles by electron microscopy, however, yielded rather uncertain results. Only within the past 10 years has purification been sufficiently successful to permit characterization of the virus particles.[1] Bachrach and Schwerdt, starting with brains and spinal cords of polio infected cotton rats, obtained small quantities of purified virus with which they were able to correlate infectivity with spherical particles of 27 mμ diameter viewed by electron microscopy. Studies in which tissue culture served as the source of virus for purification were continued at the University of California Virus Laboratory by the author in collaboration with Dr. C. E. Schwerdt. Approximately 360 liters of tissue culture fluid were used for each of the three antigenic types of poliovirus.

Purification

The purification procedure employed consisted of several steps to concentrate the virus and to remove non-viral contaminants. The virus was first precipitated from tissue culture fluid with methanol at *p*H 4 in the cold and collected by filtration with the aid of Celite. A saline eluate of the precipitate was then extracted with butanol to denature some of the contaminating proteins and to remove lipids. The next step was centrifugation in the preparative ultracentrifuge to collect the virus and other macromolecules in a pellet. After suspension of the pellet in saline and relatively low speed centrifugation to remove insoluble materials, the preparation was treated with the enzymes ribonuclease and deoxyribonuclease to hydrolyze contaminating nucleic acids. The nuclease treatment was then followed by a second cycle of ultracentrifugation.

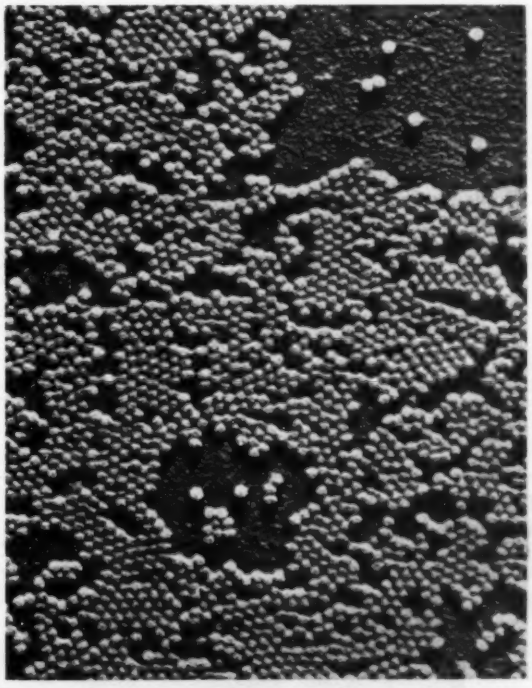

Figure 1. Electron micrograph of Type 2, strain MEF_1, poliovirus, 67,000× (2).

At this point it was found by electrophoretic and ultracentrifugal analysis that the preparation did not consist of a single homogeneous particulate component, and further purification was necessary. This was achieved by sedimentation in a density gradient in the swinging cup rotor of the ultracentrifuge. The preparation was layered over a previously prepared gradient of sucrose solutions and subjected to a field of about 78,000 times gravity for 2 hours. Light scattering bands were visualized in the gradient, and es-

The work here reported was supported in part by the National Foundation. Presented at the Joint Meeting of the Pacific Southwest Association of Chemistry Teachers, California State Polytechnic College, San Luis Obispo, California, January 3, 1959.

[1] Procedures and results of purification of poliovirus and studies of physico-chemical properties of the virus have been reviewed elsewhere (*2, 3*), and these reviews may be consulted for more extensive details and references.

sentially all the infectivity was associated with the heaviest band.

The results of the purification indicated recoveries from 10–80% of the virus from the original fluid with volume concentration factors of 10,000–50,000-fold. The yield was about 0.1 mg of highly purified virus per liter of tissue culture fluid which originally contained about 100 mg of protein. Because of the expense and limited amounts of material available, micro-techniques were employed in the analysis and characterization of the purified particles.

Physical Properties

The electron microscope has been a powerful tool in virus research for determining the size and shape of particles, their homogeneity, and freedom from gross contaminants. An electron micrograph of purified Type 2 poliovirus is shown in Figure 1. The particles appear to be spherical in shape with a diameter of 27 mμ where close packed. The isolated particles are somewhat flattened upon drying. The particles of poliovirus Types 1 and 3 were indistinguishable from Type 2 by electron microscopy.

The sedimentation constant of the virus has been measured in the analytical ultracentrifuge. In addition to sedimentation in ordinary aqueous media, sedimentation studies were made in heavy water, D_2O, to determine the dry weight density of the particles. This information coupled with the estimate of the size and shape of the particles by electron microscopy has allowed us to calculate the mass or molecular weight of the particles. Table 1 presents a summary of these data.

Table I. Some Physical Properties of Highly Purified Poliovirus, from Hydrodynamic Studies and Electron Microscopy

Type strain	1 Mahoney	2 MEF-1	3 Saukett
S (Svedbergs)	160	158	157
Dry density, g/cc	1.57	1.56	1.62
Diameter, mμ	27.3	27.0	27.2
Molecular weight	6.8×10^6	6.8×10^6	6.4×10^6
Particle mass, g	1.13×10^{-17}	1.12×10^{-17}	1.08×10^{-17}
Water of hydration, g H_2O/g dry weight	0.30	0.28	0.37

Chemical Properties

All viruses studied to date have contained both protein and nucleic acid, the nucleic acid being either of the ribose or deoxyribose type. According to current knowledge developed largely in the Virus Laboratory, the nucleic acid is responsible for infectivity and genetic continuity. The protein probably forms a protective coating and is responsible for the antigenic nature of the virus. In addition, some animal viruses also contain lipids and carbohydrates. The ultraviolet absorption spectrum of poliovirus was typical of that of a nucleoprotein with rather high nucleic acid content. The indole test for deoxyribose was negative, while the orcinol test for pentose indicated a ribonucleic acid content of about 25–30%. This value was compatible with the phosphorus content and the ultraviolet extinction coefficient. Further analyses of the nucleic acid portion of the virus have been made after hydrolysis and chromatography of the constituent bases, adenine, guanine, cytosine, and uracil. The results indicated that the ratios of these bases were not significantly different among the three types of virus, thus the differences in antigenic type must reside in something more subtle than the gross composition of the genetic material. Further studies are being pursued to learn more about the protein component of the virus. Although complete analyses have not been made, it appears that the virus contains neither lipid nor carbohydrate other than the ribose of the nucleic acid.

Figure 2. Single crystal of Type 1, strain Mahoney, poliovirus, 100× (4).

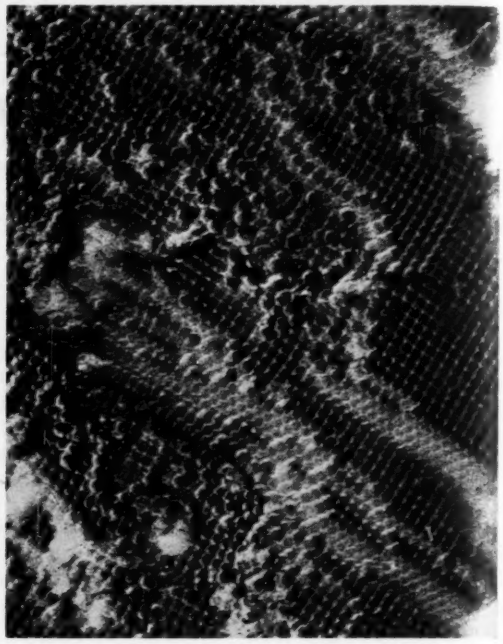

Figure 3. Electron micrograph of a replica of a fractured frozen crystal of Type 1, strain Mahoney, poliovirus showing various planes within the crystal, 63,000× (4).

Crystallization

Poliovirus was the first virus that infects humans or animals to be crystallized although a number of plant viruses had previously been crystallized. In 1955 crystals of the MEF_1 strain of Type 2 virus were obtained from an ultracentrifugally prepared pellet. Subsequently crystals of Mahoney strain of Type 1 virus formed spontaneously upon storage of a concentrated preparation. These were larger and better

formed than the earlier crystals and were amenable to further study. Figure 2 shows an isolated crystal from that preparation.

The internal packing of the particles in the Mahoney crystals was determined by electron microscopy. To do this the crystals were frozen and then fractured with a knife. Carbon replicas of the exposed surfaces were prepared and examined in the electron microscope. An area of such a surface is shown in Figure 3. Both square-packed and hexagonally-packed planes of particles are seen. Other crystals fractured only along hexagonally close packed planes. The observed packing was compatible with face centered cubic symmetry of the particles within the crystals and with external measurements that indicated a cube-octahedron habit within the isometric system. These crystals have also been submitted for analysis by X-ray crystallography. Such studies should not only shed further light on the packing of particles within the crystals, but what is more important, they should reveal information on the structure of the individual particles themselves.

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High School Students as Research Assistants

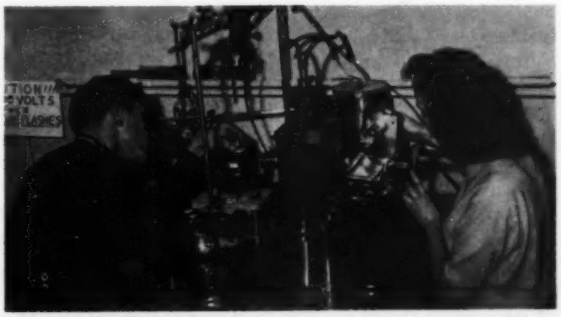
Research by the faculty members of small liberal arts colleges need not be curtailed because of an inadequate budget for the remuneration of research assistants. Faced with a minimum budget and with the utter lack of graduate student assistants, the authors found that the use of high school young people as summer research assistants was completely satisfactory.

One of the authors had the assistance of two boys and a girl in a project involving a study of directional catalysts useful in cyanoethylation of phenol. Working three-hour shifts they quickly learned how to assemble apparatus such as closed-system stirring assemblies, vacuum distillation setups, and a pressure reaction vessel made from pipe and scrap metal. Laboratory operations were modified to make best use of the combination of the high level of interest and the low level of specific chemical knowledge possessed by the young people. After detailed instructions were written on the blackboard and the use of apparatus was demonstrated they were capable of following through with dispatch and accuracy.

A second project, a problem of phase modifications in crystals of the *n*-aliphatic amide series, utilized an additional boy and girl, both high school freshmen. Working in the mornings, five days each week, they helped mount crystalline samples and align them in the X-ray diffraction cameras, develop the X-ray film, and reload the cameras. The tedious task of measuring diffraction patterns was carried out with eagerness and a high degree of precision.

The five young people worked from mid-June until mid-August, showing great interest and patience no matter at what pace the research proceeded. At no time was an effort made to provide any special stimulus to their enthusiasm and no remuneration was paid them. In each stage of the research the students were entirely trustworthy and scientifically reliable. Sincerity and interest marked their attitudes all summer long. One boy felt so near his work that he asked, apologetically, for an excuse to make a two-day camping trip. One of the girls was so engrossed in her part in the project that she took baby-sitting jobs at night in order to earn her bus fare from home to the college. A field trip to a local chemical plant climaxed the summer, serving to illustrate the application of research in industrial problems.

The authors feel that the students gained an insight into a non-glamorous side of science while the authors were gaining valuable assistance. In the end the research advanced at no cost to the budget. And the young people expressed a desire to start again the following summer.



High school students Jay Larson and Lynne Mathis operating X-ray diffraction equipment.

Report of the New England Association of Chemistry Teachers

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The Growth of Lead Trees in Silicic Acid Gels

The fact that more active metals, such as zinc and cadmium, will replace lead in solutions of lead salts is well known to students in college and high school. It is not so well known that the lead deposited will form an attractive, tree-like growth. These trees are fragile, but, if supported in a gel, they may be kept for a long time. These experiments are easily carried out and provide good projects, especially for high school students. In addition, the literature is not extensive and much remains to be discovered concerning the growth and form of these "trees."

Probably the first to mention growing trees in silicic acid gels was Simon (*1*). Holmes (*2*) also described the growth of trees, especially in his well known laboratory manual (*3*) where one experiment was described. Stone (*4*) has described similar trees, not grown in gels, and Brewington (*5*) has given a brief discussion with photographs.

In the article by Taft and Starek (*6*), excellent photographs are given, together with a good discussion on the effects of many factors. This article should be read, if possible. The method of taking photographs is described. One can obtain a good idea of the effect of many factors on the growth of these trees from this article, but it is difficult to devise and perform experiments, guided by the article, unless one has had experience.

The inverted character of these trees has led Fillinger (*7*) to report on a method of growing them right-side-up. King and his associates (*8*) have written several articles on the general subject of lead trees in gels, with emphasis on the morphology of the trees. Persons interested will find a few other articles on the shape of lead growths deposited by displacement, or electrolytically.

It seems to us that a useful function will be performed and work in this field will be stimulated if we describe several experiments which can be performed successfully by anyone interested. Our research on this whole subject has convinced us that these simple experiments offer a good introduction to the study of this subject.

Brief remarks on the theory are sufficient here since previous articles have discussed it. The tree forms because a more active metal replaces lead in the form of its ions in the gel. The lead metal deposits on the more active metal, while atoms of the more active metal go into solution as ions. The deposited lead "grows" in a crystalline form towards sources of lead ions not yet replaced. The crystalline form results because the lead deposits slowly. The gel supports the crystalline growth or tree. So long as the advancing end of the tree has metallic connection to the active metal, the point of deposition can be at some distance from the point where the active metal is dissolving. It is only necessary that the electrons flow through the metal to the point where they are needed, i.e., the advancing end of the tree branch.

Others, such as Taft and Starek, have discussed the electrochemistry involved. Obviously, the more active metal must have a greater tendency to dissolve, forming ions, than does the lead. This tendency will depend on the metal's standard potential and that of the lead, together with the concentration of the ions of each. The hydrogen ion concentration is important since it may prevent formation of basic salt or oxide layers on the metal. Ions which will produce insoluble salts with either metal interfere, although we shall describe one experiment where an insoluble salt is involved.

The silicate and the gel are important. Formation of bubbles in the gel may distort or break the tree. We have had best results with gels at *p*H 4–5. The silicate must be poured into the acid solution, for gels in this *p*H range, to give good gels free from clots.

Formation of a Simple Tree. Dilute sodium silicate (water glass) to a sp gr of about 1.06 with distilled or demineralized water, although tap water will work. Our best results have been with "C" brand silicate made by the Philadelphia Quartz Company. If 120 ml of glacial acetic acid are diluted to 1.0 liter, the solution is approximately 2.0 *N*. For a 1.0 *N* lead acetate solution, dissolve 190 g solid C.P. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ and make up to 1.0 liter.

Place 5 ml of lead acetate solution in 20 ml of the 2 *N* acetic acid and mix. Pour *into this*, 20 ml of the silicate; mix by pouring back and forth, and pour into an 8-in. test tube. When the gel is set, pour 5–10 ml distilled water on the top, insert a clean piece of zinc, and cork the tube. A good tree, very bushy near the top in contact with the zinc but growing down through the tube, will form.

Variations. By using lower concentrations composed of a smaller volume of the 1 *N* solution, made up to 5 ml, you will observe the effect of the lead ion concentration. For lower concentrations, the tree will be less bushy, will grow more slowly, but will probably form better crystals.

Variation in the Active Metal. Although zinc is usually used for the active metal, an interesting project, especially for high school students' work, is to vary the metal. Iron, even nails, tin, cadmium, magnesium, and a number of others will work.

We have noted a difference in the type of tree produced. With zinc, the tree is bushier, with iron more slender and clearly defined. With tin, we have found that the main stem and branches are planar.

Variation of Acidity of the Gel. Best results are obtained with acidic gels. By using less acid in the 20 ml, making up the difference with distilled water, one will obtain less acidic gels. We have found that tree growth ceased when the gel had a pH = 7. The variation in the type of tree is worth noting as the pH is changed. Students should note that the basic gels are more milky. This is partly due to the gel itself, partly, probably, to basic insoluble lead salts being formed.

Growth of Tree Through Precipitate. If the regular gel is prepared but dilute sulfuric acid, 1 *N* or even more dilute, is placed on top before the zinc is thrust into the gel, a curious result is produced. The sulfate ions penetrate the gel, forming a white, milky layer of lead sulfate. Through this, the lead tree will grow. Since the tips of the tree are constantly pushing farther into the gel, they deplete the lead ions before sulfate ions can reach them. Thus, a white band forms at the top, but this stops while the tree grows down through the whole tube.

This experiment will suggest many combinations and can serve as an interesting project. It is well not to use too strong sulfuric acid above the gel, or the tree may be destroyed. The use of salts, such as sodium sulfate in solution, is thus suggested.

Variation of the Metal Replaced. Although the title of this article mentions "lead" trees, others are possible. Lead appears to give by far the best tree-like growth, but a search for others should prove interesting. Taft and Starek (*6*) offer some suggestions.

Tubes containing trees may be kept for a long time if the solution remaining at the top is poured off after the tree is formed and is replaced by more water or very dilute acid. More active metal should be placed on top. The cork should fit tightly so that the water is not lost. A paraffin or wax seal around the stopper will help keep the water in the tube. We have kept some trees 10 years.

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A Modified Water Rheostat

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A modified water rheostat apparatus, as shown in the figure, may be easily constructed from two pieces of glass tubing (2 × 50 cm and 3.5 × 40 cm) and copper wire electrodes (3 mm diameter). Variable voltage is obtained at the heater, stirrer, etc., by changing the distance between the two electrodes. The upper movable electrode is covered and insulated by a small piece of glass tubing. Spiral wire electrodes are recommended in order to lessen coverage of the electrode surface by the precipitates formed during the electrolysis.

Using a 750-watt heater, a 20% sodium chloride solution, and an input voltage of 100 volts, variable voltages between 15 and 75 volts were obtained. Similar voltages were obtained from a 300-watt heater and a 4% sodium chloride solution.

Advantages of this modified water rheostat include its small size, inexpensiveness, lack of splashing, low rate of evaporation of the salt solution (less than 1 ml/1 hr), constant temperature of the salt solution during operation, and an essentially constant voltage obtained at the heater or stirrer. A large Liebig condenser may be used in place of the two pieces of glass tubing.

Modified water rheostat. *A*, cooling water; *B*, NaCl solution; *E*, electrode; *R*, heater or stirrer, etc.

Chem Ed

LETTERS

To the Editor:

Since our paper "Predicting Failures in General Chemistry" was published in this Journal, **35**, 507 (1958), we have received a great many letters requesting reprints and specific information.

The Iowa Chemistry Aptitude Test is available from the Bureau of Educational Research and Service, Extension Division, State University of Iowa, Iowa City, Iowa.

The Toledo Chemistry Achievement Test has been replaced by the Toledo Chemistry Placement Examination. This new examination became available early this summer. For information and prices, write The Research Foundation, University of Toledo, Toledo 6, Ohio.

The Iowa Aptitude Test is suitable for testing students who have not had high school chemistry. The Toledo Chemistry Placement Examination is specifically designed for testing students with credit in high school chemistry in order to determine which ones should be denied admission to the regular general chemistry course in college or university.

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Albertine Krohn

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To the Editor:

The paper of Burrell on "Balancing Organic Redox Equations" in the February issue called to mind the earlier, quite extensive discussions of this problem in THIS JOURNAL. A summary and bibliography of the early comments and the most general method for balancing any equation, redox or otherwise, are given by Bennett, THIS JOURNAL, **31**, 324 (1954). As Bennett points out, the "Oxidation Number" and "Ion-Electron" methods of balancing equations are useful because they are more convenient and quicker than the general method. While the method proposed by Burrell may have some validity from a mechanistic viewpoint in a number of cases (WALLING, C., "Free Radicals in Solution," John Wiley & Sons, Inc., New York, **1957**, chapter 11), in view of the somewhat involved rules required and the necessity of finding the change in oxidation number of the oxidant, I think that the claim that this method allows balancing by *inspection* is overoptimistic. Unless a better understanding of the true mechanism of the reaction being studied is obtained, the use of this new method will only serve to complicate the problem.

In particular, the application of this method to the oxidation of $K_4Fe(CN)_6$ by MnO_4^- ion in acid solution seems to me to be a step backward. If the products quoted in this example are correct, which I doubt, since ferrocyanide can be titrated to ferricyanide in acid solution with permanganate, the substances taking part in the reaction (hydrated forms being disregarded) would be $Fe(CN)_6^{-4}$, H^+, MnO_4^-, Fe^{+3}, NO_3^-, CO_2, Mn^{++}, and H_2O. To ask the student to think of the presence of KOH, $Fe(OH)_2$, $Fe(OH)_3$, and unionized HNO_3 is to undo the work of the general chemistry course.

A comparison of the reduction steps used by Burrell written in ionic form with the commonly used half reactions shows that what has been done is to simply leave out the electrons. This has the effect of changing OH^- ions, if the reaction takes place in alkaline solution, or H_2O molecules in acid solution, to OH radicals when charge equality between reactants and products is preserved. For example:

$$3e^- + MnO_4^- + 2H_2O \rightarrow MnO_2 + 4OH^-$$
$$MnO_4^- + 2H_2O \rightarrow MnO_2 + OH^- + 3OH$$

$$5e^- + MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O$$
$$MnO_4 + 3H^+ + H_2O \rightarrow Mn^{++} + 5OH$$

$$6e^- + Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O$$
$$Cr_2O_7^{-2} + 8H^+ \rightarrow 2Cr^{+4} + H_2O + 6OH$$

Incidentally, although Burrell states that a perfect material balance has been obtained without the use of ionic forms in his table of oxidizing agents, a mole of water is missing from the reactant side in the reaction of $KMnO_4$ in acid solution, and a mole of water is missing from the product side in the reaction of $K_2Cr_2O_7$ in acid solution. Perhaps these omissions were oversights. With reference to the oxidation steps proposed, the same comments apply to the reciprocal relationship of electrons and OH radicals.

Actually the balancing of organic redox reactions can be carried out quite readily by the ion-electron method taught in many general chemistry courses as shown by the following examples.

(A) The oxidation of propylene in alkaline solution for which the over-all molecular equation is

$$C_3H_6 + KMnO_4 \rightarrow CH_3COOK + K_2CO_3 + MnO_2 + KOH + H_2O$$

The reduction step is the usual half reaction of MnO_4^- ion in alkaline solution,

$$3e^- + MnO_4^- + 2H_2O \rightarrow MnO_2 + 4OH^-$$

The oxidation step is

$$C_3H_6 + 13OH^- \rightarrow CH_3COO^- + CO_3^{-2} + 8H_2O + 10e^-$$

Certainly in alkaline solution, the predominant species are acetate and carbonate ions, not the acids. After the usual cross multiplication, addition, and cancellation of excess substances, the final result is

$$3C_3H_6 + 10MnO_4^- \rightarrow 3CH_3COO^- + 3CO_3^{-2} + 10MnO_2 + OH^- + 4H_2O$$

If the molecular equation is desired, 10 K^+ ions can be added to each side giving

$$3C_3H_6 + 10KMnO_4 \rightarrow 3CH_3COOK + 3K_2CO_3 + 10MnO_2 + KOH + 4H_2O$$

(B) The oxidation of 1-menthol to 1-Menthone by dichromate in dilute sulfuric acid:

$$C_{10}H_{20}O + K_2Cr_2O_7 + H_2SO_4 \rightarrow C_{10}H_{18}O + Cr_2(SO_4)_3 + H_2O$$

The reduction step in this case is

$$6e^- + Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O$$

The oxidation step is

$$C_{10}H_{20}O \rightarrow C_{10}H_{18}O + 2H^+ + 2e^-$$

no organic ions being involved. Again multiplication, addition, and cancellation result in the final ionic equation,

$$3C_{10}H_{20}O + Cr_2O_7^{-2} + 8H^+ \rightarrow 3C_{10}H_{18}O + 2Cr^{+3} + 7H_2O$$

Again, if the molecular equation is preferred, 2 K^+ ions and $4SO_4^{--}$ ions must be added to each side giving.

$$3C_{10}H_{19}O + K_2Cr_2O_7 + 4H_2SO_4 \rightarrow 3C_{10}H_{18}O + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

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To the Editor:

The merit of Professor Gaddis' "Titration Without Burets," THIS JOURNAL **36**, 290 (1959), will be considerably enhanced if the solutions are weighed on a rough balance to the nearest tenth of a gram, neglecting bouyancy corrections. One anticipates a precision of ±0.5% being obtained in this way. Weighing to within 0.010 g with bouyancy corrections should easily surpass the accuracy of an ordinary buret.

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BOOK REVIEWS

Some Problems of Chemical Kinetics and Reactivity. Volume I

N. N. Semenov, Academy of Sciences of the U.S.S.R. Translated by *J. E. S. Bradley*. Pergamon Press, Inc., New York, 1959. x + 305 pp. 31 figs. 39 tables. 15 × 22.5 cm. $7.50.

Some Problems in Chemical Kinetics and Reactivity. Volume I

N. N. Semenov. Translated by *Michel Boudart*. Princeton University Press, Princeton, N. J., 1958. xii + 239 pp. Figs. and tables. 15 × 22.5 cm. Paper bound. $4.50.

The original book by Semenov was published in 1954 by the Academy of Sciences of the U.S.S.R., and was an expanded version of the opening paper for a conference on Chemical Kinetics and Reactivity. The translations listed above were prepared in collaboration with the author and incorporate certain revisions and new data. The original book contained nine chapters. Both translations are partial and a further volume is promised in each case. Bradley's translation contains seven of the nine chapters and Boudart's six. The translations are of equal merit and the reader can choose which he prefers. Bradley's is bound in hard covers, is well printed, on good paper, has an author index, a subject index and one chapter more than Boudart's. Boudart's has soft covers, is a reproduction of a typed manuscript on poor paper, and has no indexes. The Bradley translation costs half as much again and in the opinion of the reviewer is worth it. For reasons mentioned below, the book is of a type which makes it very valuable to Western readers, and the translation of Russian works like this is of the greatest importance. It seems a most unnecessary waste of effort that two English translations of the same book should appear practically simultaneously. Both translations were made in collaboration with the author, and it is hard to believe that the translators were unaware of each other's efforts. It is certainly to be hoped that a similar waste of effort will not be too frequent in the future.

The book consists of four parts. Part I is on Radical Reactions (Propagation and Branching of Chain Reactions), and contains three chapters: Uniradical Reactivities; Alternative Univalent Free Radical Reactions; The Reactions of Biradicals. Part II is on the Initiation and Termination of Chain Reactions, with chapters on Molecular Dissociation and Radical Combination, Ions as Chain Initiators, and Wall Initiation and Retardation. Part III on the Kinetics of Chain Reactions is represented by one chapter in Bradley's book, and is not represented in Boudart's. Bradley's translation also contains appendixes on The Activated Complex and on The Quantum Mechanical Calculation of Activation Energies.

The book is of great value and is a "must" for all laboratories working in the field. Professor Semenov's contributions are of great importance. In recent years there has been rather a split in outlook between Western work and that in Semenov's institute. This is particularly marked in questions of interpretation of reactions of alkyl radicals, especially those involving hydrogen-abstraction reactions. As a result it is of particular importance that Semenov's point of view be available to Western workers. In a number of cases the reviewer disagrees strongly with the conclusions. The fact that such disagreement is possible, however, makes the availability of the book in the West of prime importance. Translations such as this can do much to help overcome the barriers between work in Russia and in the West, and the book is thus a most valuable account of the opinions of the major school of chemical kinetics in the U.S.S.R.

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Soviet Research in Catalysis. Volumes 1–7

Chemistry Collection No. 3. Consultants Bureau, Inc., New York, 1959.
Vol. 1: Theoretical and Sundry Associated Effects. 265 pp.
Vol. 2: General. 257 pp.
Vol. 3: General. 253 pp.
Vol. 4: General, Reduction, Oxidation, Fischer-Tropsch. 225 pp.
Vol. 5: Hydrogenation, Dehydrogenation, Cracking. 297 pp.
Vol. 6: Isomerization, Alkylation, Dehydration. 275 pp.
Vol. 7: Polymerization, Friedel-Crafts, Zeigler. 129 pp. Figs. and tables. 21.5 × 27 cm. Paper bound. Volumes 1–6, $50 each. Vol. 7, $30. The set, $200.

The contents of this set consist of articles in the field of catalysis from Russian journals which have been previously translated into English and published by Consultants Bureau. The original Russian journals are: *Journal of Applied Chemistry, Bulletin of the Academy of Sciences, Journal of General Chemistry*. The original publication dates in Russian range from 1949 to 1955, so it is well over ten years since some of this work was done in the laboratory. This extended time lag, as well as the high cost of commercial translations, should be a powerful incentive for scientists to master the art of reading scientific Russian.

The range of subject matter and quality of these papers is wide. They have been roughly organized according to subject. However, some of the subjects listed on the title pages seem a little optimistic. For example, under polymerization one finds only three articles: one on decomposition of oleic acid, one on decomposition of styrene oxide, and one on polymerization of isobutylene vapors on quartz. A polymer chemist might be disappointed by this showing. Some of the other titles listed also show this weakness.

The general subject areas which are listed are: theoretical, general, reduction, oxidation, Fischer-Tropsch, hydrogenation, dehydrogenation, cracking, isomerization, alkylation, dehydration, polymerization, Friedel-Crafts, and Ziegler.

Reviewed in this Issue

N. N. Semenov, Some Problems of Chemical Kinetics and Reactivity. Volume 1
Soviet Research in Catalysis. Volumes 1–7.
A. I. M. Keulemans, edited by *C. G. Verver*, Gas Chromatography
D. H. Desty, Editor, Gas Chromatography 1958
J. A. A. Ketelaar, Chemical Constitution
W. F. Luder, Arthur A. Vernon, and *Saverio Zuffanti*, General Chemistry
Louis F. Fieser and *Mary Fieser*, Basic Organic Chemistry
Louis Gordon, Murrell L. Salutsky, and *Hobert H. Willard*, Precipitation from Homogeneous Solution
John C. Sheehan, Editor-in-Chief, Organic Syntheses. Volume 38
Herbert W. Cremer and *Trefor Davies*, Editors, Chemical Engineering Practice. Volume 5
C. Kittel, Elementary Statistical Physics
Franz E. Hohn, Elementary Matrix Algebra
Forman S. Acton, Analysis of Straight-Line Data
E. Paskell, Editor, Semiconductor Abstracts. Volume 4
W. G. Wyckoff, Crystal Structure. Supplement 4.

Each volume has a table of contents, but has no index nor is there an overall index. The utility of the set would be increased if such indexes were available.

The range of the work is an indication of the vigor of Russian work in chemistry. It is to be hoped that more effective contact between Russian and American chemists will become more common so that both may benefit.

The worker in the field of catalysis or organic chemistry will almost certainly find something of interest in this set. Whether the high purchase price can be justified will depend on the individual situation.

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Gas Chromatography

A. I. M. Keulemans, edited by *C. G. Verver*, Research Chemists, Koninklijke-Shell-Laboratorium, Amsterdam. Reinhold Publishing Corp., New York, 1957. xix + 217 pp. Many figs. and tables. 16 × 23.5 cm.

In the opinion of the reviewer, this book will be the bible of gas chromatographers for many years to come.

Dr. Keulemans, of the Koninklijke/Shell Laboratorium, is one of the pioneers in gas chromatography, and has published a number of papers in this field. In keeping with current practice, he has devoted most of his book to gas-liquid chromatography, and only a single chapter to gas-solid chromatography.

The arrangement of topics seems very good. An introductory chapter is followed by one on analytical applications of gas-liquid chromatography. Operating variables are discussed here, and some examples of typical separations are presented. Qualitative and quantitative methods are included also.

Chapters 4, 5, and 6 cover the theoretical aspects of gas-liquid chromatography. Special applications are discussed in Chapter 7. A section here on the design of columns for difficult separations will be much appreciated.

The book concludes with a chapter on gas-solid chromatography. Three appendixes discuss stationary liquids, katharometers, and the purification of commercial carbon dioxide. An author index completes the volume.

The style is clear, yet concise. Although a beginner should have little difficulty in following the book, the material is complete enough to satisfy the more advanced worker. The literature has been covered through 1955, with some references to papers presented at the London Symposium in 1956.

The book lacks a subject index, but the very detailed Table of Contents provides a reasonably good substitute.

Anyone who works with gas chromatography will find this book indispensable. It is recommended without reservation.

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Gas Chromatography 1958

Edited by *D. H. Desty*. Academic Press, Inc., New York, 1959. xiii + 383 pp. Many figs. and tables. 16.5 × 25.5 cm. $13.

This book contains the Proceedings of the Second Symposium on Gas Chromatography under the auspices of the Hydrocarbon Research Group of the Institute of Petroleum and the Netherlands Chemical Society held in Amsterdam in May, 1958.

The 28 papers are conveniently grouped into three sections: Theory (10 papers), Techniques and Apparatus (9 papers), and Applications (9 papers). Each section is preceded by a brief review by the section chairman. Opening and closing addresses, a summary of the symposium, and a short report on nomenclature are also included. A discussion follows most of the papers.

Much of the early work in gas chromatography was largely empirical. Papers in this symposium, however, make it clear that theory is catching up with practice, and that the design of very efficient columns based on theoretical considerations is now possible.

Among the new developments discussed here might be mentioned wetted-wall capillary columns and several detectors of high sensitivity. Undoubtedly advances of this kind will find wide acceptance (at least one gas chromatographic unit which uses a capillary column and an ionization detector is already on the market). The newer detectors have prompted A. T. James to observe in his summary, "It may well be that the day of the katharometer is nearly over."

This book is a valuable addition to the rapidly growing literature on gas chromatography. It should be especially useful to research workers and to those interested in the design and application of instruments, but even the occasional user of gas chromatographic techniques will find much to interest him. The nonmathematician will have some rough going in several of the theoretical papers, but the nature of the material makes this unavoidable. Many good ideas are presented in the course of the discussions, and the reader is urged not to overlook them.

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Chemical Constitution

J. A. A. Ketelaar, Professor of Physical Chemistry, the University of Amsterdam. 2nd ed. Elsevier Publishing Co., New York, 1959. Sole Distributors, D. Van Nostrand Co., Inc., Princeton, N. J. viii + 448 pp. 35 figs. 37 tables. 16 × 23 cm. $8.95.

The new edition of Ketelaar's "Chemical Constitution" represents a welcome addition to the array of texts available in the area of structural theory. While it does not differ greatly from the previous edition, it is obvious that the numerical data, particularly in the tables, and the literature references have been brought up to date and many new subjects are mentioned or discussed, although briefly. The book's greatest strength, its coverage of a tremendously wide area in a thoroughly systematic fashion (under four main headings, the ionic, atomic, metallic bonds, and Van der Waals bonding) seems to be simultaneously its greatest weakness since no subject is discussed in sufficient detail to more than whet the reader's appetite. In many areas the American reader is exposed to approaches with which he is likely to be relatively unfamiliar, since Ketelaar has drawn very strongly on the continental European literature, sometimes almost to the exclusion of alternate American theory. Since American books frequently suffer from an analogous preference for work native to this country, Ketelaar's book should serve a very useful purpose in presenting points of view new to the reader; the same characteristic, however, will probably keep the book from finding wide acceptance as a text.

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General Chemistry

W. F. Luder, Arthur A. Vernon, and *Saverio Zuffanti*, Professors of Chemistry, Northeastern University. 2nd ed. W. B. Saunders Co., Philadelphia, 1959. xvii + 582 pp. 149 figs. 110 tables. 16.5 × 24 cm. $6.75.

The new second edition of this well-known textbook presents an improved and very pleasing appearance. The extra-large boldface type used for all formulas and equations is particularly effective.

Changes over the first edition appear to be rather minor. There is a minimum of rewriting and some rearrangement of chapters. A brief history of chemistry has been switched from Chapter 1 to a section of fine print in the appendix.

Users of the first edition will be pleased to find many new problems as well as some revision of old ones. Answers are given for some of the problems. Supplementary reading references and summary questions are also provided for each chapter.

Organic chemistry is introduced earlier (Chapters 19 and 20) and treated more extensively than is customary in other current texts. Carbohydrates, fats, and proteins receive separate consideration near the end of the book. Polymerization, rubber, rubber substitutes, and plastics also have their own chapter.

Solutions of electrolytes get more than the usual attention and the electronic theory of acids and bases is emphasized.

Atomic orbitals are mentioned briefly but the authors prefer to explain chemical bonding in terms of "valence electrons" which are rather arbitrarily defined. It may startle some chemists to read that copper has eleven "valence electrons" while iron has only eight. The molecular orbital theory is not mentioned.

Evidently, these authors subscribe to that old adage "if you can't lick 'em,

(*Continued on page A528*)